

2017

Speciation, Distribution, Prediction, and Mobility of Lead in Urban Soils: A Multiscale Study

Jennifer Bower
University of Vermont

Follow this and additional works at: <https://scholarworks.uvm.edu/graddis>



Part of the [Environmental Health and Protection Commons](#), [Geochemistry Commons](#), and the [Geology Commons](#)

Recommended Citation

Bower, Jennifer, "Speciation, Distribution, Prediction, and Mobility of Lead in Urban Soils: A Multiscale Study" (2017). *Graduate College Dissertations and Theses*. 715.
<https://scholarworks.uvm.edu/graddis/715>

This Thesis is brought to you for free and open access by the Dissertations and Theses at ScholarWorks @ UVM. It has been accepted for inclusion in Graduate College Dissertations and Theses by an authorized administrator of ScholarWorks @ UVM. For more information, please contact donna.omalley@uvm.edu.

SPECIATION, DISTRIBUTION, PREDICTION, AND MOBILITY OF LEAD IN
URBAN SOILS: A MULTISCALE STUDY

A Thesis Presented

by

Jennifer A. Bower

to

The Faculty of the Graduate College

of

The University of Vermont

In Partial Fulfillment of the Requirements
for the Degree of Master of Science
Specializing in Geology

May, 2017

Defense Date: March 21, 2017
Thesis Examination Committee:

Nicolas Perdrial, Ph.D., Advisor
Donald S. Ross, Ph.D., Chairperson
Andrew W. Schroth, Ph.D.
Cynthia J. Forehand, Ph.D., Dean of the Graduate College

ABSTRACT

Lead (Pb), a trace metal notorious for its impacts on human health, has achieved worldwide environmental dispersal resulting from centuries of use by human society. The toxicity of Pb is governed largely by its mineral form, which is in turn controlled by pH, localized reactivity and soil processes that differ according to soil type, location and Pb source. Given the context of these localized dependencies, or site specificity, efforts to predict Pb toxicity and refine sustainable remediation techniques are most useful when Pb behavior is constrained and predicted within environments with homogeneous conditions, such as a single soil. I evaluated and predicted the behavior of Pb, a typical anthropogenic contaminant, within a single soil using bioaccessibility testing and predictive geospatial modeling to assess potential impacts and refine sustainable remediation methods. To test the hypothesis that Pb speciation is influenced by competitive sorption processes in soils, I investigated changes in mobility and speciation of Pb upon addition of amendments at multiple scales using flow-through column experiments, soil characterization and synchrotron-based x-ray techniques.

Kriging and cokriging maps provided a successful estimation of background and total Pb, the latter incorporating housing age as a secondary variable to increase model accuracy, though efforts to automate detection of background Pb were complicated by approximation of building extents, and overall heterogeneity of soil Pb concentration gives high error. Acute Pb heterogeneity is observed at the scale of a single site among near-structure samples. At the city-scale, determination of bioaccessibility revealed that bioaccessible and total Pb are well-correlated, to the extent that bioaccessibility may be predicted for the soil underlying Burlington, VT; this information, combined with predictive blood lead level modeling and the CDC's recent establishment of $5 \mu\text{g kg}^{-1}$ as a threshold for blood lead toxicity, enabled the establishment of a site-specific revised soil Pb limit of 360 mg kg^{-1} , lower than the EPA's general soil Pb threshold of 400 mg kg^{-1} .

Characterization of leached and unleached soil using scanning electron microscope energy dispersive spectroscopy (SEM-EDS) and microfocused x-ray techniques provided a first look at Pb paint species using synchrotron technologies. Pb was present within paint chips as hydrocerussite, but appeared to weather to anglesite over time. Pb also seemed to act as cation bridge, attracting clay minerals electrostatically and becoming incorporated into heterogeneous soil aggregates. Accessory paint elements are identified in soil and within paint chips and may further complicate these systems. Column experiments, at acidic pH, yielded little evidence of Pb mobility change in response to modification of competitive sorbents. Kinetics of Pb release were driven by pH, with Pb solubilizing at pH of ~ 4.9 as column soil acidifies.

This work provides evidence for changes in Pb speciation over time in urban soils impacted by Pb paint, and presents a framework for predictive risk analysis at a local site using experimental and modeling tools. Multiscale observations and analytical results can be used in future efforts to model and refine sustainable remediation solutions within a site-specific context.

CITATIONS

Material from this thesis has been submitted for publication to *Environmental Pollution* on January 31, 2017 in the following form:

Bower, J.A., Lister, S., Hazebrouck, G., & Perdrial, N.. (in review). Geospatial evaluation of lead bioaccessibility and distribution for site-specific prediction of threshold limit. *Environmental Pollution*.

ACKNOWLEDGEMENTS

This work would not have been possible without the patience and generosity of many. I would like to thank first and foremost Nico Perdrial, for his mentorship and thoughtful scientific approach. His enthusiasm for addressing questions big and small using creative technologies and student-driven inquiry inspires many, and I am no exception.

I am grateful to my committee members, who expanded the potential of this work, and to the faculty and graduate students who provided encouragement, pizza, talk therapy, and advice. Our dearly departed departmental fish soothed my teaching nerves with his mournful and placid stare.

The encouragement of friends and family was a major catalyst for this work, and I particularly appreciate my parents' tolerance for alternating intervals of groaning and rejoicing. Most remarkably, they never asked, "Why geology?"

Finally, I am deeply thankful to my partner Jas, who was a willing audience for every spoken presentation, cheerfully endured many science-related exclamations at the dinner table, and heard me give the elevator version of this work more times than I have friends. I open my eyes so I can see with you.

TABLE OF CONTENTS

Page	
CITATIONS.....	ii
ACKNOWLEDGEMENTS.....	iii
TABLE OF CONTENTS.....	iv
LIST OF FIGURES	vi
LIST OF TABLES	viii
CHAPTER 1: Introduction and Comprehensive Literature Review	1
1.1. Introduction.....	1
1.2. Literature Review	7
1.3. References	17
CHAPTER 2: Geospatial Evaluation of Lead Bioaccessibility and Distribution for Site Specific Prediction of Threshold Limits	28
2.1. Introduction.....	30
2.2. Materials and Methods	34
2.3. Results.....	39
2.3.1. Total Pb distribution	39
2.3.2. Measured and predicted bioaccessibility.....	39
2.3.3. Pb geolocation and techniques for multiscale distribution modeling.....	40
2.4. Discussion and Conclusions.....	44
2.5. References	52
2.6. Artwork	56
2.7. Tables	60
CHAPTER 3: Competitive Sorption Dynamics Control Lead Behavior in an Urban Soil at Multiple Scales.....	61
3.1. Introduction.....	62
3.2. Materials and Methods	66
3.3. Results and Discussion	70
3.4. References	81
3.5. Tables	85
3.6 Figures	87
CHAPTER 4: Concluding Remarks and Future Work.....	94

CHAPTER 5: Comprehensive Reference List	98
CHAPTER 6: Supplemental Figures	113

LIST OF FIGURES

CHAPTER 1: Introduction and Comprehensive Literature Review	
Figure 1. Yearly tonnage of Pb dispensed in gasoline and paint within the US (Mielke, 1999; Filippelli, 2005).....	2
Figure 2. Pb bioavailability as a function of species and particle size (Drexler and Brattin, 2007; modified from Ruby et al., 1999)	5
Figure 3. Stability diagram showing unstable nature of Pb carbonates and oxides at low pH, in comparison to chloropyromorphite (Hopwood et al., 2002).....	10
CHAPTER 2: Geospatial Evaluation of Lead Bioaccessibility and Distribution for Site Specific Prediction of Threshold Limits	
Figure 1. Extractable (bioaccessible) vs. total Pb within contaminated Burlington soils. Transparent symbols represent in vitro bioavailable Pb (IVBA), non-adjusted; opaque symbols represent relative bioavailability, adjusted from IVBA using weighted linear regression. Regression formula and r^2 value represent RBA values only.	56
Figure 2. (a) Total Pb distribution in Burlington and surrounding areas. (b) Background Pb distribution in Burlington and surrounding areas. (c) Kriging interpolation showing predicted total Pb distribution in Burlington soil, with sample locations symbolized in black. (d) Cokriging interpolation showing distribution of background Pb in Burlington soil, with sample locations symbolized in black.	57
Figure 3. (a) Site-specific inverse data weighting (IDW) interpolation map showing total Pb distribution at two similar structures, with measured concentrations given by circles graduated with increasing Pb concentration and predicted concentrations symbolized by contours. Structure on the left was built in 1880; structure on right was built in 1899. (b) Predicted site-specific health burden of children age 1-2 at two similar structures.	58
Figure 4. Burlington structures with a predicted maximum health burden exceeding CDC threshold of $5 \mu\text{g dL}^{-1}$	59
CHAPTER 3: Competitive Sorption Dynamics Control Lead Behavior in an Urban Soil at Multiple Scales	
Figure 1. a. Representation of contaminant metal (gray sphere) behavior within soil microenvironments in an example soil pore space (quartz dominated). Red arrows represent flow direction. b. Specific behavior at soil microsites affecting Pb ions in solution.	87
Figure 2. a (upper left). pH over time (PV = Pore Volume) within columns leached with acidified rainwater and acidified rainwater modified with PO_4 , respectively; both were conducted at pH of 3 and unamended with goethite. Figure 2b (lower left). Pb concentration over time within columns mentioned in 2a. Figure 2c (upper right). pH over time within columns leached with PO_4 and amended with various goethite ($\text{FeO}[\text{OH}]$) preparations, all conducted at pH of 3. Figure 2d (lower right). Pb concentration over time within columns mentioned in 2c.	88

Figure 3. Concentration of various elements within column experiment effluent; Pb concentration is subtracted from total estimated Pb to give estimated fraction Pb remaining.....	89
Figure 4. a, b. Microscale SEM-EDS images of soil particles within unleached column; c. Microscale SEM-EDS images of soil particles within column leached with PO ₄ -amended rainwater and amended with FeO(OH). Scale bar represents 50 μm.....	90
Figure 5. Combined μXRF map, with Pb given in green, K in blue, and Fe in red, within column leached with PO ₄ -amended rainwater.....	91
Figure 6. Top: Combined μXRF map, with Pb given in green, Zn in blue, and Fe in red, within column leached with PO ₄ -amended rainwater. Locations where significant μXRD patterns of Pb minerals were collected are given by white dots and labeled with pattern number. Bottom: Comparisons between μXRD pattern collected from sample (top pattern) and reference mineral (lower pattern) for samples 13-04-01 and 13-04-09.....	92
Figure 7. Diagram showing relative stability of PbCO ₃ (cerussite) and derivative species (PbSO ₄ [anglesite], Pb Pb ₅ [PO ₄] ₃ Cl [chloropyromorphite], and PbHPO ₄ [lead hydrogen phosphate]) in an aqueous system in the presence of SO ₄ ²⁻ , Fe ²⁺ , HCO ₃ ⁻ , and Cl ⁻ , all ions with activities of 1.0, in response to changing pH and log HPO ₄ ²⁻	93
CHAPTER 6: Supplemental Figures	
Figure 1. Location of sites remediated by the Burlington Lead Program, symbolized according to age of housing and ownership status. Data obtained from the City of Burlington, visualized using QGIS and OpenStreetMaps.....	113
Figure 2. Housing age of residential parcels in Burlington and surrounding areas of Chittenden County.....	114
Figure 3. Site-specific IDW interpolation map showing differences in bioaccessibility at two structures, with measured values given by circles and predicted symbolized with contours.....	114
Figure 4. Experimental setup and configuration of flow-through column experiments.....	115
Figure 5. Zoomed-out SEM image encompassing area where SEM-EDS was conducted in Chapter 3, Figure 7, with Figure 7 extent demarcated by red boundary box.	116
Figure 6. Elemental correlations for μXRF map 17-01 (unleached soil), with r correlations given in top of each box.	118
Figure 7. Expanded synchrotron-collected μXRF maps of column leached with PO ₄ -amended rainwater depicted in Chapter 3, Figure 6, with lighter shades corresponding to fluorescence: Pb, Zn, Fe and U. U is included as it fluoresces in trace quantities within the polygonal mineral (probably a feldspar) on the right side of the map, rendering this mineral visible.	118

LIST OF TABLES

CHAPTER 2: Geospatial Evaluation of Lead Bioaccessibility and Distribution for Site-Specific Prediction of Threshold Limit	
Table 1. Total Pb distribution statistics for samples gathered near Burlington, Vermont.	60
CHAPTER 3: Competitive Sorption Dynamics Control Lead Behavior in an Urban Soil at Multiple Scales	
Table 1. Rainwater preparations used for column experiments.....	85
Table 2. Column preparations and replicates.....	85
Table 3. Characteristics of soil selected for use in columns.	86
Table 4. Bioaccessibility of Pb in unleached soil and after column experiments.....	86

CHAPTER 1: Introduction and Comprehensive Literature Review

1.1. Introduction

Human activity has irrevocably impacted the geochemistry of Earth's surface, resulting in changes in geochemical cycling observed below the lower boundary of the critical zone to the highest reaches of our atmosphere. Whether mining and redistributing crustal trace elements such as Pb, Cu, and U, or introducing cement, plastics and other relics of human activity into urban soil fabrics, humanity has played a large role in changing the biogeochemical landscape in which we currently live (Steffen, 2016). Understanding the fate and behavior of geochemical markers of the Anthropocene is key for understanding the complex nature of these changes and corresponding impacts on human health and the environment.

The complicated relationship between human civilization and environmental contaminants is well represented by the rise and fall of lead, a persistent neurotoxin that was exploited within a range of applications and continues to affect human health worldwide, representing the most widespread toxin on the planet (Hong et al., 1994; Marx et al., 2016). Used widely by the Romans within infrastructure and even culinary applications, to the extent that Pb is believed to have played a role in the downfall of the Roman civilization (Nriagu, 1983), Pb was subsequently mined for use in paint, solder, shipbuilding, and ammunition, for its properties of high opacity and durability and given that it was cheap to obtain. Due to a broadening array of applications in industry, manufacturing and paint, the mining and exploitation of this trace element initiated large-scale deposition of Pb in soil, water, and the atmosphere. In the 20th century, DuPont decided to patent the use of Pb as a gasoline additive to prevent engine

knocking instead of a simpler cellulose-derived compound due to the inability of the company to patent the latter (Filippelli et al., 2005). Advertising campaigns promoting Pb products reinforced public perception of Pb as a beneficial chemical to society. It is estimated that $5\text{-}6 \times 10^6$ t of Pb was used to manufacture paint in the U.S. (Mielke and Reagan, 1998), roughly the same amount used within gasoline, before it was banned in 1978 through the passage of the Lead-Based Paint Poisoning Prevention Act (Johnson et al., 2011). In the 1960s, the work of isotope geochemist Clair Patterson contributed to the discovery that Pb levels were accumulating worldwide as a result of human activity (Murozumi et al., 1969) and later, that these levels posed significant risks to human health (Settle and Patterson, 1980). In the ensuing years, notwithstanding fierce opposition from industry stakeholders, regulations were enacted to phase out the use of lead in paint, solder, and finally gasoline (Figure 1). Despite these reforms, Pb

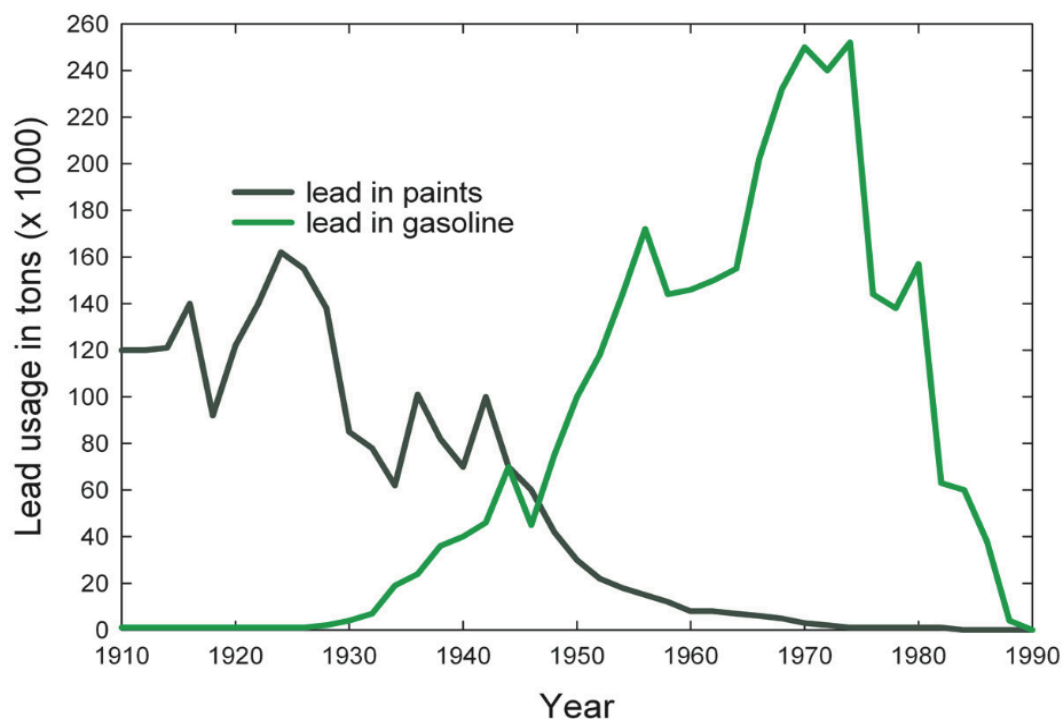


Figure 1. Yearly tonnage of Pb dispensed in gasoline and paint within the US (Mielke, 1999; Filippelli, 2005).

continues to pose a hazard to human health due to its long residence time and toxicity.

Before Pb was identified as a danger to public health, paint pigments were dominated by Pb (as well as Zn), as Pb carbonate was thought of as a complete pigment. This led to heavy Pb enrichment within older paint formulations, up to 650 mg g⁻¹, as determined through acid extraction (Hunt, 2016). Alone, Pb was added to paint in several carbonate forms, including PbCO₃, 2PbCO₃·Pb(OH)₂, and 4PbCO₃·2Pb(OH)₂·PbO. When used in combination with other pigments, Pb was added as various compounds of PbSO₄. Accessory elements (Mg, Zn, Ba, Cr, Fe) were added to produce various colors or to act as filler. Once Pb was banned for use in paint, TiO₂ was substituted within modern paint formulations. Differences in speciation within paint are accompanied by different morphologies; Pb particles are observed in spherical, angular, irregular or acicular form according to their composition, which likely leads to differences in reactivity within soil (Hunt, 2016). Morphological behavior of Pb paint has thus been studied recently at the microscale post-paint application (and after mixing with soil), but has not yet been examined within soil contaminated by historical inputs of Pb from paint using microfocused techniques.

The principal negative health impacts of Pb are rooted in the ability of Pb ions to substitute for Ca in the human body within neurotransmitters and bones, due to a similarity in ionic radii and charges. When Pb substitutes for Ca in the former scenario, it impedes neurotransmission and impairs neurological growth, especially within children. In the latter scenario, once incorporated into the structure of hydroxyapatite, bone can act as a long-term source of Pb to the affected person, effectively prolonging the harm of initial exposure (Filippelli and Laidlaw, 2010). Children bear the brunt of

negative effects from Pb exposure, as they absorb Pb at a far higher rate than adults once it is introduced to their system, due to their small size and less developed gastrointestinal tracts (Laidlaw et al., 2016). They are also more likely to ingest Pb from hand to mouth behavior and play activity (Taylor et al., 2013). Although Pb may be taken in from a variety of pathways and sources, including water, air, and food, the highest risk of transmission is from dust and soil, which harbor historical Pb contributions from paint and gas (Clark and Knudsen, 2013; Lanphear et al., 1998; Mielke et al., 1997). The high electronegativity of Pb yields strong bonds between Pb ions and soil sorbents, with Pb having particular affinity for iron oxides and oxyhydroxides, free anions, and organic matter functional groups, the latter preference giving Pb a typically long residence time in soils, on the order of 60-150 years in montane forests (Kaste, 2003). Lead speciation is controlled locally at the molecular level by equilibrium-dependent reactions and localization of reactive sites. When considered as discrete zones, areas of varying reactivity may be termed microenvironments, and, when aggregated, dictate the behavior of Pb at the field scale (Hesterberg et al., 2011). In turn, Pb speciation, along with physical characteristics such as particle size and aggregation, determines bioavailability, or the extent to which Pb is absorbed by organisms, as shown in Figure 2 (Drexler and Brattin, 2007; Ruby et al., 1999).

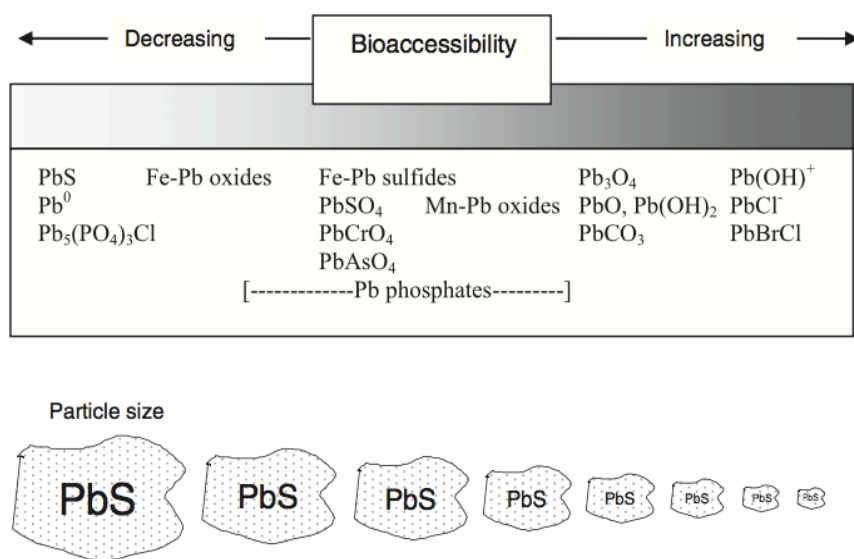


Figure 2. Pb bioavailability as a function of species and particle size (Drexler and Brattin, 2007; modified from Ruby et al., 1999)

Given the dependence of Pb speciation and bioavailability on localized soil chemistry and soil characteristics, establishment of a unified threshold for maximum soil Pb to assess risk potential across soils and contamination sources seems unrealistic. In this vein, recent work by Henry and others (Burt et al., 2014; Henry et al., 2015; Zheng et al., 2013) has identified a need for assessing Pb within a site-specific framework. By incorporating factors including soil type, Pb speciation, mineralogy, and bioaccessibility into assessment, site-specific studies may lead to the development of recommendations regarding local hazard risk and the refinement of sustainable remediation solutions (Von Lindern et al., 2003). Phosphate amendment, a technique built on the insolubility of Pb phosphate minerals, has been identified as a compelling candidate for remediating Pb impacted soil. However, this process-based approach is currently impractical due to the recalcitrance of Pb to coprecipitate with phosphate within field scenarios of varying geochemical conditions, believed to result from

competitive sorbent behavior and the occupation of Pb and phosphate binding sites by other soil constituents (Debela et al., 2013; Hashimoto et al., 2009).

This thesis is comprised of two studies that are nested within the larger work. Within the first chapter (submitted as a standalone manuscript to Environmental Pollution, Bower et al., [in review]) I hypothesize that for an area comprised of a unified soil type and a primary Pb source, the factors controlling Pb behavior affect Pb similarly throughout the soil area such that bioaccessibility and risk can be predicted in untested areas. This work relates quantitative characterization of local soil Pb to evaluation of community health impacts at multiple scales using applied geospatial and public health techniques. Once replicated within another soil type, this framework can be implemented in other cities to identify and target sites and neighborhoods where the risk of Pb is greatest. Pb was found to be spatially heterogeneous at different scales, while geochemically it behaved somewhat predictably. To this end, I established a site-specific threshold for acceptable soil Pb for a local area through bioaccessibility assessment and risk-based predictive modeling of Pb risk within an urban community with older housing. This can then be used to aid in the development of targeted remediation and hazard assessment by local organizations.

In the second paper, I examine whether competitive behavior hinders the efficiency of $\text{PO}_4\text{-Pb}$ sorption in near-field environments. This is tested by examining the response of Pb to increases in competitive sorbents within near-field phosphate-amended systems to understand the nature of Pb heterogeneity within soil systems at multiple scales. As part of this inquiry I present the first effort to characterize Pb speciation within soil impacted by Pb paint through microfocused x-ray techniques,

hypothesizing that hydrocerussite is the principle paint species affecting this soil and is unstable relative to its surroundings. Using these analyses, along with supplemental observations gained through SEM-EDS and bench-scale experimentation, I investigate the role of Pb in urban soil fabrics, and present implications of Pb species transformations in paint-impacted soil.

1.2. Literature Review

The behavior and mobility of Pb in soils is determined by equilibrium-dependent reactions, biological activity, and soil weathering factors, which affect the form or species of Pb. Adsorption processes, both reversible and irreversible, represent the main driver of Pb sequestration in natural soils (Morin et al., 1999; Serrano et al., 2009), with Pb reactivity dominated by interactions between organic matter, iron oxides and oxyhydroxides, and clay minerals (Vidal et al., 2009). In soils, Pb is present primarily within the Pb(II) oxidation state. When under reducing conditions, Pb commonly exists as lead sulfide (PbS); under oxidizing conditions, its free ionic form (Pb^{2+}) is strongly attracted to negatively charged mineral surfaces and anionic groups (Alloway, 2012). As a result, oxygen ligands within functional groups on organic matter bind Pb tightly through electrostatic bonds and inner-sphere complexes (Strawn and Sparks, 2000; Xia et al., 1997). Surface hydroxyl groups on iron oxides and oxyhydroxides bind with Pb through adsorption and coprecipitation (Martinez and McBride, 1999; Morin et al., 1999), while clays incorporate Pb ions within interlayer space as well as to negatively charged edges (Sipos et al., 2008). In addition, free anions such as phosphate or sulfate groups form complexes or coprecipitate with Pb to

form minerals given conditions congruent with mineral stability and availability of anions (Porter et al., 2004). Finally, certain organisms may impact Pb speciation, such as soil nematodes and bacteria, which transform Pb to a less soluble form during the digestive process (Jackson et al., 2005; Perdrial et al., 2008), and buckwheat, which has been observed to have a solubilizing effect on Pb (Hashimoto et al., 2011a). Pb speciation varies according to depositional source, and alters according to local geochemical conditions. Pb-bearing jarosites and Fe-Pb adsorbates predominate at sites impacted by mine tailings (Ostergren et al., 1999); shooting ranges contain metallic Pb altering to hydrocerussite and small quantities of anglesite (Cao et al., 2003);

Presently, the only unified and reliable method for soil Pb remediation consists of removing and disposing of affected soil. This “dig and dump” strategy is expensive, given the cost of removal and transportation to a containment facility, and unsustainable, as the practice of discarding soil jeopardizes an increasingly precious natural resource (Hodson, 2010). *In situ* techniques, which use soil amendments to reduce the solubility of Pb or harness the ability of plants or fungi to uptake Pb in place, represent an attractive alternative to soil disposal (Scheckel et al., 2013). Biochar and compost amendments make use of the strong affinity of Pb for organic matter, and may reduce the extent to which Pb is mobile in soils and available to plants (Tandy et al., 2009; Uchimiya et al., 2010; Xie et al., 2015); however, the extent to which they decrease Pb bioavailability to humans is attributed to a dilution effect (Attanayake et al., 2015) and some uses may actually increase metal mobilization (Park et al., 2011). Phytoremediation and mycoremediation rely on the specific ability of certain fungi and plant species such as *Brassica juncea* (Indian mustard) to hyperaccumulate Pb, drawing

it out of the soil (Blaylock et al., 1997). For this method to be effective, site conditions must be suitable for growing and Pb must be in a bioavailable form. Once it has absorbed the contaminant, the organism must be removed from the site (Dickinson et al., 2009), or it reenters the soil again, occasionally in a more labile form, when the organism decays.

Soil-forming factors affect Pb speciation over time, especially given that the form in which Pb is introduced to soil may be unstable relative to the geochemical environment of the surrounding soil (e.g. when lead carbonate species are introduced to an acidic soil). Examination of anthropogenic Pb deposits from ancient Roman settlements (57 B.C. – 350 A.D.), combined with research indicating soluble forms of Pb quickly transform to less soluble species in soil and air after deposition, indicates that Pb species partition to recalcitrant forms over time, decreasing the extent to which Pb is available for absorption by organisms (Laxen and Harrison, 1977; Schroth et al., 2008; Walraven et al., 2016; Walraven et al., 2015). In the case of mineral transformations, particle size, aggregation, and encapsulation effects create zones of heterogeneous speciation, as evidenced by the formation of hydrocerussite crusts on lead bullets at firing ranges (Cao et al., 2003; Rooney et al., 2007; Vantelon et al., 2005). These soil processes also affect binding partners of Pb, as iron oxides and hydroxides become less effective sorbents over time (Ford et al., 1997). Local pH affects the partitioning of Pb species (Ostergren et al., 1999; Shahid, 2012); increasing pH increases the likelihood of Pb precipitating as sulfate, carbonate, or phosphate species, sorb to mineral or oxide, or complex with organic matter, all species that possess varying solubility according to thermodynamic properties and pH (Reeder et

al., 2006; Ruby et al., 1999). Stability diagram of Pb across pH regimes is given in Figure 3. The extent to which Pb is absorbed by organisms, specifically humans, is expressed as bioavailability, a parameter that is presented as a fraction to indicate the proportion of total Pb absorbed. Pb bioavailability is dependent on species, with low-solubility forms of Pb exhibiting correspondingly low bioavailability (Chaney et al., 1989; Ruby et al., 1992; Ruby et al., 1999; Traina and Laperche, 1999). Airborne pollutants such as NO₂ and O₃ can alter the solubility of Pb, with increased exposure leading to higher availability (Edwards et al., 2009). The development of sustainable *in situ* process-based remediation methods has focused on the transformation of soluble Pb species to more insoluble forms to reduce the extent to which they are absorbed by

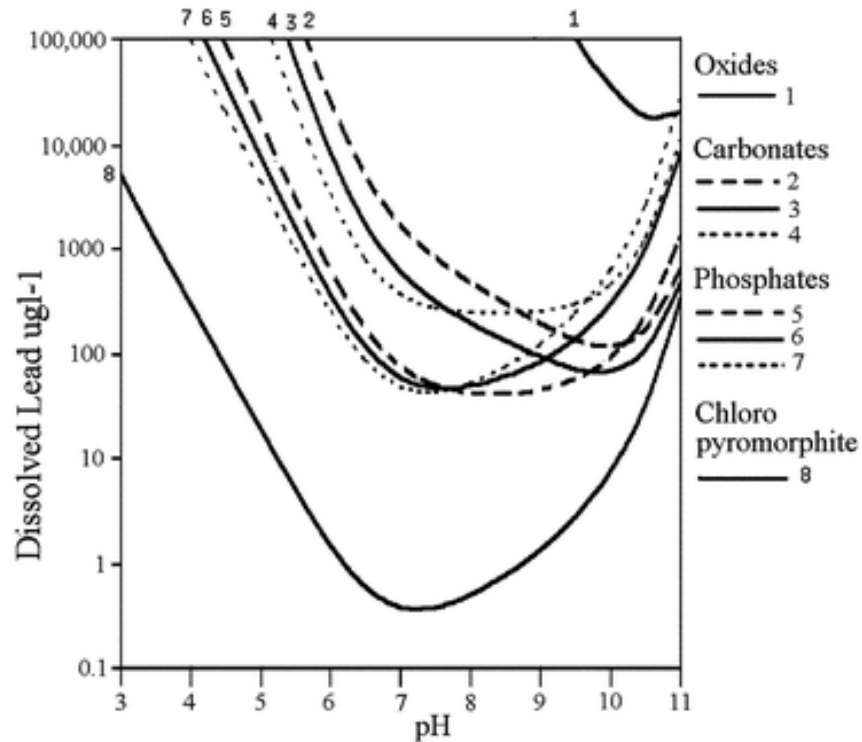


Figure 3. Stability diagram showing unstable nature of Pb carbonates and oxides at low pH, in comparison to chloropyromorphite (Hopwood et al., 2002).

organisms (Hettiarachchi et al., 2000; Kumpiene et al., 2008; Miretzky and Fernandez-Cirelli, 2008).

Within soil systems comprised of organic matter, metal oxides and silicate minerals, Pb tends to bind to the fine fraction and exhibits a strong preference for organic matter (Alloway, 2012; Cancès et al., 2003; Perdrial et al., 2010). Pb may bind with organic matter and to hydroxyl groups on iron oxides and oxyhydroxides at neutral and near-neutral pH but primarily complexes to organic matter within acidic regimes (Tessier et al., 1996; Vermeer and Koopal, 1999). Associations between iron oxides and oxyhydroxides and Pb are composed of bidentate and monodentate inner sphere complexes, with the former dominating under alkaline conditions (Bargar et al., 1998; Trivedi et al., 2003), the strength of these bonds contributing to a reduction in the solubility of Pb (de Miguel et al., 2012). Fe oxides and oxyhydroxides readily bind to soil organic matter, an association predicated on the attraction between oxide and oxyhydroxide surface charge and functional groups on organic matter (Chorover and Amistadi, 2001). The availability of binding sites on organic matter and Fe oxides and oxyhydroxides is affected by binding of oxides and organic matter to each other as well as competitive behavior between Pb and other metals as they vie for available reactive sites (Negra et al., 2005; Sauve et al., 2000). This can affect Pb in various ways: by removing available sites for Pb to bind to, causing it to be available for binding with other sorbents such as anion groups or acquire greater mobility due to lack of binding partners; by Pb preferentially sorbing weakly at certain reactive sites and desorbing once pH changes or a stronger binding partner is found; by Pb and other paint metals competing with each other for reactive sites, with behavior of Pb (or Ti, or Zn, etc.)

determined by the outcome of competition. When multiplied, these microscale dynamics can control field-scale behavior of Pb (Hesterberg et al., 2011).

Pyromorphite, a lead phosphate mineral, has exceedingly low solubility and correspondingly low bioaccessibility compared to other Pb species, of which chloropyromorphite ($\text{Pb}_5[\text{PO}_4]_3\text{Cl}$) is the most thermodynamically stable across a range of pH conditions (Nriagu, 1973, 1974), and is found naturally within soils given an available source of phosphorus (Cotter-Howells and Caporn, 1996). In a laboratory setting, several studies achieved promising rates of pyromorphite formation when phosphate was applied to soil (Brown et al., 2004; Hettiarachchi et al., 2003). The variability of Pb behavior within different soils, according to Pb source (Manceau et al., 1996), and in response to competitive behavior complicates the effectiveness of phosphate remediation techniques (Hashimoto et al., 2009) and renders outcomes of phosphate remediation unpredictable at the field scale. In some cases, strong sorption of Pb to Fe oxides and organic matter leaves it unavailable for binding to PO_4 ; the binding of PO_4 to Fe oxides, organic matter, and other soil constituents can also present an impediment to Pb- PO_4 coprecipitation (Debela et al., 2013; Hiemstra et al., 2013). The presence of PO_4 can enhance sorption of Pb to Fe oxides and oxyhydroxides, implying ternary complexation between Pb, PO_4 , and Fe oxides (Tiberg et al., 2012). The greatest effect of PO_4 remediation is observed when PO_4 is added in an exceedingly soluble form such as liquid phosphorus or diammonium phosphate (Scheckel et al., 2013; Schwab et al., 2006; Yoon et al., 2007), however this is likely to be a cause of concern in areas afflicted by high PO_4 burdens within water sources, such as Vermont (Chrysochoou et al., 2007; Miretzky and Fernandez-Cirelli, 2008; Scheckel et al.,

2013). Soil may be acidified or amended with EDTA to increase the availability of Pb for binding to PO_4 (Su et al., 2015), but this also renders Pb more soluble for organismal uptake and increases the potential for Pb to leach into nearby waterways (Bolan et al., 2014; Shahid et al., 2012). Though useful in immobilizing Pb, PO_4 amendment has the secondary consequence of rendering As more soluble, an issue in areas affected by dual As and Pb burdens (Cui et al., 2010; Impellitteri, 2005).

Pb species are difficult to constrain using traditional analytical methods; traditional sequential extraction methods are susceptible to forming pyromorphite during extraction, leading to overestimation of sampled pyromorphite (Scheckel et al., 2013). Furthermore, Pb species are typically not present in high enough concentrations within bulk soil samples to be discernible through powder x-ray diffraction (XRD) analysis of bulk soil; synchrotron-based microfocused XRD is better equipped to analyze crystalline Pb species, as this technique allows microscopic identification of minerals (Baker et al., 2014). Methods to measure and predict the extent to which soil lead is absorbed consist of two main types: *in vivo* tests to measure Pb bioavailability directly within organisms, and *in vitro* tests which estimate Pb bioaccessibility through simulated digestion of Pb impacted soil under low pH conditions and estimate organismal bioavailability by subjecting bioaccessibility measurements to mathematical adjustment (Drexler and Brattin, 2007; Hettiarachchi and Pierzynski, 2004). *In vitro* digestions consist of simplified acidic extractions simulating digestion within the gastric phase, or multiphase extractions that include saliva, gastric, and intestinal phase steps. Past work has noted the superfluity of including additional phases beyond the gastric phase, as smaller proportions of Pb are absorbed at other steps and a less

conservative estimate of Pb is achieved, leading to underestimation of bioavailability (Deshommes et al., 2012). Simple gastric digestions exhibit strong correlation with absolute bioavailability as established through validation with *in vivo* testing, and therefore represent the most suitable *in vitro* method for conservatively estimating bioavailability (EPA, 1999; Rasmussen et al., 2011). Sequential extraction has been used to estimate partitioning of Pb between recalcitrant and soluble fractions, but these methods may underestimate soluble Pb and risk forming recalcitrant Pb phases during extraction; Clark et al. used sequential extraction to estimate the proportion of bioavailable Pb within paint-impacted soils to be 1.8%, conceding that this represented an underestimate (Clark et al., 2008). Estimates of relative bioavailability of paint-derived Pb as derived from *in vitro* extraction techniques are higher, ranging from 37.2-100.0 within historical paint samples composed primarily of Pb carbonates, to 75 ± 18 within urban home dust likely sourced from Pb paint (Hunt, 2016; Rasmussen et al., 2011). Pb is less bioavailable within soils contaminated by smelter activity and mine tailings, as primary minerals consist of recalcitrant lead oxide and sulfate phases, and bioavailability is generally controlled by dissolution of the anglesite fraction, an alteration product of galena (Hemphill et al., 1991). Information from bioavailability assessment can be used to estimate risk to humans, especially children, using integrated predictive models such as the EPA's Integrated Exposure Uptake Biokinetic, a tool that incorporates average burdens from diet, water, air, and play activities to predict Pb concentration in blood given total Pb content and bioavailability as inputs (Glorennec and Declercq, 2007; White and Marcus, 1998).

Bioaccessibility prediction and blood lead level modeling can be used in conjunction with survey of total Pb to tailor remediation and characterization of anthropogenic Pb to a single site with a single soil type. Pb bioaccessibility can vary widely according to Pb source and soil characteristics; therefore, this site-specific approach enables Pb behavior to be constrained according to local Pb sources and soil environment, such that remediation can be better targeted according to the bioaccessibility and species of Pb in the soil. The geology of the site selected for this study is comprised of lower and middle Cambrian metasedimentary units, of the Dunham Dolostone and Monkton Quartzite formations, overlaid by glaciolacustrine and glaciofluvial sediment deposited 13,500 to 12,000 years ago, as well as artificial fill deposited by humans during heyday of industrial activity in Burlington and Winooski (Ratcliffe, 2011; Wright et al., 2009). The primary soil within this area is the Windsor series, a loamy sand. Mean concentration of Pb in Chittenden County, as analyzed by the National Geochemical Survey within stream sediments (considered authigenic for the general purposes of this work), is 27.1 mg kg^{-1} ($\pm 3.6 \text{ mg kg}^{-1}$) (USGS, 2004).

The provenance of anthropogenic Pb within soil and humans by Pb source (i.e. gasoline-derived, weathered from paint, or deposited from smelting or mining operations) has previously been constrained through geospatial and isotopic means. Isotopic analysis of Pb absorbed by humans and within the environment is used to assess the influence of individual Pb sources in areas with multiple overlapping inputs (Glorennec et al., 2010; Linton et al., 1980; Oulhote et al., 2011; Semlali et al., 2001). Geospatial methods have identified the source and extent of local Pb through interpolation models, buffer analysis and through comparative analysis of parcel

characteristics, including age and proximity to roads (Clark and Knudsen, 2013; Miranda et al., 2011; Morrison et al., 2013; Schwarz et al., 2012; Wu et al., 2010). Assessment of Pb bioavailability and sitewide risk is also performed through geospatial means (Cattle et al., 2002; McGrath et al., 2004; Saby et al., 2006). Synchrotron-based methods represent a unique opportunity for characterizing the impact of Pb sources through examination of microspatial distribution of Pb and determination of Pb species (Baker et al., 2014; Hashimoto et al., 2011b; Kirpichtchikova et al., 2006; Scheckel and Ryan, 2004; Smith et al., 2011; Vantelon et al., 2005). To date, Pb behavior in soil from paint has not yet been studied in this way using microfocused x-ray techniques.

1.3. References

- Alloway, B. J., Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability. Springer Netherlands: 2012.
- Attanayake, C. P.; Hettiarachchi, G. M.; Martin, S.; Pierzynski, G. M., Potential bioavailability of lead, arsenic, and polycyclic aromatic hydrocarbons in compost-amended urban soils. *Journal of Environmental Quality* 2015, 44, (3), 930.
- Baker, L.; Pierzynski, G.; Hettiarachchi, G.; Scheckel, K.; Newville, M., Micro- X- Ray Fluorescence, Micro- X- Ray Absorption Spectroscopy, and Micro- X- Ray Diffraction Investigation of Lead Speciation after the Addition of Different Phosphorus Amendments to a Smelter-Contaminated Soil. *Journal of Environmental Quality* 2014, 43, (2), 488-497.
- Bargar, J. R.; Brown, G. E.; Parks, G. A., Surface Complexation of Pb(II) at Oxide-Water Interfaces: III. XAFS Determination of Pb(II) and Pb(II)-Chloro Adsorption Complexes on Goethite and Alumina. *Geochimica et Cosmochimica Acta* 1998, 62, (2), 193-207.
- Blaylock, M. J.; Salt, D. E.; Dushenkov, S.; Zakharova, O.; Gussman, C.; Kapulnik, Y.; Ensley, B. D.; Raskin, I., Enhanced accumulation of Pb in Indian mustard by soil-applied chelating agents. *Environmental Science & Technology* 1997, 31, (3), 860.
- Bolan, N.; Kunhikrishnan, A.; Thangarajan, R.; Kumpiene, J.; Park, J.; Makino, T.; Kirkham, M. B.; Scheckel, K., Remediation of heavy metal(loid)s contaminated soils – To mobilize or to immobilize? *Journal of Hazardous Materials* 2014, 266, 141-166.
- Brown, S.; Chaney, R.; Hallfrisch, J.; Ryan, J. A.; Berti, W. R., In situ soil treatments to reduce the phyto- and bioavailability of lead, zinc, and cadmium. *Journal of Environmental Quality* 2004, 33, (2), 522-531.
- Burt, R.; Hernandez, L.; Shaw, R.; Tunstead, R.; Ferguson, R.; Peaslee, S., Trace element concentration and speciation in selected urban soils in New York City. *Environmental Monitoring and Assessment* 2014, 186, (1), 195-215.
- Cancès, B.; Ponthieu, M.; Castrec-Rouelle, M.; Aubry, E.; Benedetti, M. F., Metal ions speciation in a soil and its solution: experimental data and model results. *Geoderma* 2003, 113, (3), 341-355.
- Cao, X.; Ma, L. Q.; Chen, M.; Hardison, D. W.; Harris, W. G., Weathering of lead bullets and their environmental effects at outdoor shooting ranges. *Journal of Environmental Quality* 2003, 32, (2), 526.

- Cattle, J.; McBratney, A. B.; Minasny, B., Kriging method evaluation for assessing the spatial distribution of urban soil lead contamination. *Journal of Environmental Quality* 2002, 31, (5), 1576-1588.
- Chaney, R. L.; Mielke, H. W.; Sterrett, S. B., Speciation, mobility and bioavailability of soil lead. *Environmental Geochemistry and Health* 1989, (11), 105-129.
- Chorover, J.; Amistadi, M. K., Reaction of forest floor organic matter at goethite, birnessite and smectite surfaces. *Geochimica et Cosmochimica Acta* 2001, 65, (1), 95-109.
- Chrysochoou, M.; Dermatas, D.; Grubb, D. G., Phosphate application to firing range soils for Pb immobilization: The unclear role of phosphate. *Journal of Hazardous Materials* 2007, 144, (1), 1-14.
- Clark, H. F.; Hausladen, D. M.; Brabander, D. J., Urban gardens: Lead exposure, recontamination mechanisms, and implications for remediation design. *Environmental Research* 2008, 107, (3), 312-319.
- Clark, J. J.; Knudsen, A. C., Extent, characterization, and sources of soil lead contamination in small-urban residential neighborhoods. *Journal of Environmental Quality* 2013, 42, (5), 1498-1506.
- Cotter-Howells, J.; Caporn, S., Remediation of contaminated land by formation of heavy metal phosphates. *Applied Geochemistry* 1996, 11, (1), 335-342.
- Cui, Y.; Du, X.; Weng, L.; Van Riemsdijk, W. H., Assessment of in situ immobilization of lead (Pb) and arsenic (As) in contaminated soils with phosphate and iron: solubility and bioaccessibility. (Author abstract). *Water, Air, & Soil Pollution* 2010, 213, (1-4), 95.
- de Miguel, E.; Mingot, J.; Chacón, E.; Charlesworth, S., The relationship between soil geochemistry and the bioaccessibility of trace elements in playground soil. *Environmental Geochemistry and Health* 2012, 34, (6), 677-687.
- Debela, F.; Arocena, J.; Thring, R. W.; Whitcombe, T., Organic acids inhibit the formation of pyromorphite and Zn-phosphate in phosphorous amended Pb- and Zn-contaminated soil. *Journal of Environmental Management* 2013, 116, 156.
- Deshommes, E.; Tardif, R.; Edwards, M.; Sauvé, S.; Prévost, M., Experimental determination of the oral bioavailability and bioaccessibility of lead particles. *Chemistry Central Journal* 2012, 6, (1), 138.
- Dickinson, N.; Baker, A.; Doronila, A.; Laidlaw, S.; Reeves, R., Phytoremediation of inorganics: realism and synergies. *International Journal of Phytoremediation* 2009, 11, (2), 97.

- Drexler, J.; Brattin, W., An In Vitro Procedure for Estimation of Lead Relative Bioavailability: With Validation. *Human and Ecological Risk Assessment* 2007, 13, (2), 383-401.
- Edwards, R.; Lam, N.; Zhang, L.; Johnson, M.; Kleinman, M., Nitrogen Dioxide and Ozone As Factors in the Availability of Lead from Lead- Based Paints. *Environmental Science & Technology* 2009, 43, (22), 8516.
- EPA IEUBK Model Bioavailability Variable (shortsheet); 1999.
- Filippelli, G. M.; Laidlaw, M. A. S.; Latimer, J. C.; Raftis, R., Urban lead poisoning and medical geology: An unfinished story. *GSA Today* 2005, 15, (1), 4-11.
- Filippelli, G.; Laidlaw, M., THE ELEPHANT IN THE PLAYGROUND confronting lead- contaminated soils as an important source of lead burdens to urban populations. *Perspectives In Biology And Medicine* 2010, 53, (1), 31-45.
- Ford, R.; Bertsch, P.; Farley, K., Changes in transition and heavy metal partitioning during hydrous iron oxide aging. *Environmental Science & Technology* 1997, 31, (7), 2028-2033.
- Glorennec, P.; Declercq, C., Performance of several decision support tools for determining the need for systematic screening of childhood lead poisoning around industrial sites. *European Journal of Public Health* 2007, 17, (1), 47-52.
- Glorennec, P.; Peyr, C.; Poupon, J.; Oulhote, Y.; Le Bot, B., Identifying sources of lead exposure for children, with lead concentrations and isotope ratios. *Journal of Occupational and Environmental Hygiene* 2010, 7, (5), 253.
- Hashimoto, Y.; Takaoka, M.; Oshita, K.; Tanida, H., Incomplete transformations of Pb to pyromorphite by phosphate-induced immobilization investigated by X-ray absorption fine structure (XAFS) spectroscopy. *Chemosphere* 2009, 76, (5), 616.
- Hashimoto, Y.; Takaoka, M.; Shiota, K., Enhanced Transformation of Lead Speciation in Rhizosphere Soils Using Phosphorus Amendments and Phytostabilization: An X-ray Absorption Fine Structure Spectroscopy Investigation. *Journal of Environmental Quality* 2011, 40, (3), 696-703.
- Hashimoto, Y.; Yamaguchi, N.; Takaoka, M.; Shiota, K., EXAFS speciation and phytoavailability of Pb in a contaminated soil amended with compost and gypsum. *Science of the Total Environment* 2011, 409, (5), 1001-1007.
- Hemphill, C. P.; Ruby, M. V.; Beck, B. D.; Davis, A.; Bergstrom, P. D., The bioavailability of lead in mining wastes: physical/chemical considerations. *Chemical Speciation & Bioavailability* 1991, 3, (3-4), 135-148.

- Henry, H.; Naujokas, M.; Attanayake, C.; Basta, N.; Cheng, Z.; Hettiarachchi, G.; Maddaloni, M.; Schadt, C.; Scheckel, K., Bioavailability- Based In Situ Remediation To Meet Future Lead (Pb) Standards in Urban Soils and Gardens. *Environmental Science & Technology* 2015, 49, (15), 8948.
- Hesterberg, D.; Duff, M.; Dixon, J.; Vepraskas, M., X- ray Microspectroscopy and Chemical Reactions in Soil Microsites. *Journal of Environmental Quality* 2011, 40, (3), 667-78.
- Hettiarachchi, G. M.; Pierzynski, G. M., Soil lead bioavailability and in situ remediation of lead- contaminated soils: A review. *Environmental Progress* 2004, 23, (1), 78-93.
- Hettiarachchi, G.; Pierzynski, G.; Oehme, F.; Sonmez, O.; Ryan, J., Treatment of contaminated soil with phosphorus and manganese oxide reduces lead absorption by Sprague-Dawley rats. *Journal of Environmental Quality* 2003, 32, (4), 1335-45.
- Hettiarachchi, G.; Pierzynski, G.; Ransom, M., In situ stabilization of soil lead using phosphorus and manganese oxide. *Environmental Science & Technology* 2000, 34, (21), 4614-4619.
- Hiemstra, T.; Mia, S.; Duhaut, P.-B.; Molleman, B., Natural and Pyrogenic Humic Acids at Goethite and Natural Oxide Surfaces Interacting with Phosphate. *Environmental Science & Technology* 2013, 47, (16), 9182.
- Hodson, M. E., The Need for Sustainable Soil Remediation. *Elements* 2010, 6, (6), 363-368.
- Hong, S.; Candelone, J.-P.; Patterson, C. C.; Boutron, C. F., Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations. *Science* 1994, 265, (5180), 1841.
- Hopwood, J. D.; Davey, R. J.; Jones, M. O.; Pritchard, R. G.; Cardew, P. T.; Booth, A., Development of chloropyromorphite coatings for lead water pipes. *Journal of Materials Chemistry* 2002, 12, (6), 1717-1723.
- Hunt, A., Relative bioaccessibility of Pb-based paint in soil. *Environmental Geochemistry and Health* 2016, 38, (4), 1037.
- Impellitteri, C. A., Effects of pH and phosphate on metal distribution with emphasis on As speciation and mobilization in soils from a lead smelting site. *The Science of the Total Environment* 2005, 345, (1-3), 175.
- Jackson, B.; Williams, P.; Lanzirotti, A.; Bertsch, P., Evidence for Biogenic Pyromorphite Formation by the Nematode *Caenorhabditis elegans*. *Environmental Science & Technology* 2005, 39, (15), 5620-5625.

- Johnson, C. C.; Demetriades, A.; Locutura, J.; Ottesen, R. T., Mapping the Chemical Environment of Urban Areas. Wiley: 2011.
- Kaste, J., Tracing the retention and redistribution of lead and other atmospheric fallout in soils. In Friedland, A. J., Ed. ProQuest Dissertations Publishing: 2003.
- Kirpichtchikova, T. A.; Manceau, A.; Spadini, L.; Panfili, F.; Marcus, M. A.; Jacquet, T., Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. *Geochimica et Cosmochimica Acta* 2006, 70, (9), 2163.
- Kumpiene, J.; Lagerkvist, A.; Maurice, C., Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments--a review. *Waste management (New York, N.Y.)* 2008, 28, (1), 215.
- Laidlaw, M.; Filippelli, G.; Sadler, R.; Gonzales, C.; Ball, A.; Mielke, H., Children's Blood Lead Seasonality in Flint, Michigan (USA), and Soil-Sourced Lead Hazard Risks. *International Journal of Environmental Research and Public Health* 2016, 13, (4), 1-13.
- Lanphear, B.; Burgoon, D.; Rust, S.; Eberly, S.; Galke, W., Environmental exposures to lead and urban children's blood lead levels. *Environmental Research* 1998, 76, (2), 120-130.
- Laxen, D. P. H.; Harrison, R. M., The highway as a source of water pollution: An appraisal with the heavy metal lead. *Water Research* 1977, 11, (1), 1-11.
- Linton, R. W.; Natusch, D. F. S.; Solomon, R. L.; Evans, C. A., Physicochemical characterization of lead in urban dusts. A microanalytical approach to lead tracing. *Environmental Science & Technology* 1980, 14, (2), 159-164.
- Manceau, A.; Boisset, M.-C.; Sarret, G.; Hazemann, J.-L.; Mench, M.; Cambier, P.; Prost, R., Direct determination of lead speciation in contaminated soils by EXAFS spectroscopy. *Environmental Science & Technology* 1996, 30, (5), 1540.
- Martinez, C.; McBride, M., Dissolved and labile concentrations of Cd, Cu, Pb, and Zn in aged ferrihydrite-organic matter systems. *Environmental Science & Technology* 1999, 33, (5), 745-750.
- Marx, S. K.; Rashid, S.; Stromsoe, N., Global-scale patterns in anthropogenic Pb contamination reconstructed from natural archives. *Environmental Pollution* 2016, 213, 283-298.
- McGrath, D.; Zhang, C.; Carton, O. T., Geostatistical analyses and hazard assessment on soil lead in Silvermines area, Ireland. *Environmental Pollution* 2004, 127, (2), 239-248.

- Mielke, H. W.; Dugas, D.; Mielke, P. W.; Smith, K. S.; Gonzales, C. R., Associations between soil lead and childhood blood lead in urban New Orleans and rural Lafourche Parish of Louisiana. *Environmental Health Perspectives* 1997, 105, (9), 950.
- Mielke, H. W.; Reagan, P. L., Soil is an important pathway of human lead exposure. *Environmental Health Perspectives* 1998, 106, (Suppl 1), 217-229.
- Miranda, M.; Anthopolos, R.; Hastings, D., A Geospatial Analysis of the Effects of Aviation Gasoline on Childhood Blood Lead Levels. *Environmental Health Perspectives* 2011, 119, (10), 1513-1516.
- Miretzky, P.; Fernandez-Cirelli, A., Phosphates for Pb immobilization in soils: a review. *Environ Chem Lett* 2008, 6, (3), 121-133.
- Morin, G.; Ostergren, J. D.; Juillot, F.; Ildefonse, P.; Calas, G.; Brown, G. E., Jr., XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: Importance of adsorption processes. *American Mineralogist* 1999, 420.
- Morrison, D.; Lin, Q.; Wiehe, S.; Liu, G.; Rosenman, M.; Fuller, T.; Wang, J.; Filippelli, G., Spatial relationships between lead sources and children's blood lead levels in the urban center of Indianapolis (USA). *Environmental Geochemistry and Health* 2013, 35, (2), 171-183.
- Murozumi, M.; Chow, T. J.; Patterson, C., Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. *Geochimica et Cosmochimica Acta* 1969, 33, (10), 1247-1294.
- Negra, C.; Ross, D.; Lanzirotti, A., Soil manganese oxides and trace metals: competitive sorption and microfocused synchrotron x-ray fluorescence mapping. *J. Mol. Biol.* 2005, 330.
- Nriagu, J. O., Lead orthophosphates—II. Stability of chlopyromophite at 25°C. *Geochimica et Cosmochimica Acta* 1973, 37, (3), 367-377.
- Nriagu, J. O., Lead orthophosphates—IV Formation and stability in the environment. *Geochimica et Cosmochimica Acta* 1974, 38, (6), 887-898.
- Nriagu, J. O., Saturnine gout among Roman aristocrats. Did lead poisoning contribute to the fall of the Empire? *The New England Journal of Medicine* 1983, 308, (11), 660.
- Ostergren, J.; Brwn, G.; Parks, G.; Tingle, T., Quantitative speciation of lead in selected mine tailings from Leadville, CO. *Environmental Science & Technology* 1999, 33, (10), 1627-1636.

- Oulhote, Y.; Bot, B.; Poupon, J.; Lucas, J.-P.; Mandin, C.; Etchevers, A.; Zmirou-Navier, D.; Glorennec, P., Identification of sources of lead exposure in French children by lead isotope analysis: a cross-sectional study. *Environmental Health* 2011, 10, (1), 75.
- Park, J. H.; Lamb, D.; Paneerselvam, P.; Choppala, G.; Bolan, N.; Chung, J.-W., Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. *Journal of Hazardous Materials* 2011, 185, (2), 549-574.
- Perdrial, N.; Liewig, N.; Delphin, J.-E.; Elsass, F., TEM evidence for intracellular accumulation of lead by bacteria in subsurface environments. *Chemical Geology* 2008, 253, (3), 196-204.
- Perdrial, N.; Perdrial, J. N.; Delphin, J. E.; Elsass, F.; Liewig, N., Temporal and spatial monitoring of mobile nanoparticles in a vineyard soil: evidence of nanoaggregate formation. *European Journal of Soil Science* 2010, 61, (4), 456.
- Porter, S.; Scheckel, K.; Impellitteri, C.; Ryan, J., Toxic Metals in the Environment: Thermodynamic Considerations for Possible Immobilization Strategies for Pb, Cd, As, and Hg. *Critical Reviews in Environmental Science and Technology* 2004, 34, (6), 495-604.
- Rasmussen, P.; Beauchemin, S.; Chénier, M.; Levesque, C.; Maclean, L.; Marro, L.; Jones-Otazo, H.; Petrovic, S.; McDonald, L.; Gardner, H., Canadian House Dust Study: Lead Bioaccessibility and Speciation. *Environmental Science & Technology* 2011, 45, (11), 4959.
- Ratcliffe, N. M., Stanley, R.S., Gale, M.H., Thompson, P.J., and Walsh, G.J., Bedrock geologic map of Vermont. 2011, (U.S. Geological Survey Scientific Investigations Map 3184, 3 sheets, scale 1:100,000).
- Reeder, R. J.; Schoonen, M. A. A.; Lanzirrotti, A., Metal speciation and its role in bioaccessibility and bioavailability. *Reviews in Mineralogy and Geochemistry* 2006, 64, 59-113.
- Rooney, C. P.; McLaren, R. G.; Condon, L., Control of lead solubility in soil contaminated with lead shot: Effect of soil pH. *Environmental Pollution* 2007, 149, (2), 149-157.
- Ruby, M.; Davis, A.; Kempton, J.; Drexler, J.; Bergstrom, P., Lead bioavailability: Dissolution kinetics under simulated gastric conditions. *Environmental Science & Technology* 1992, 26, (6), 1242.
- Ruby, M.; Schoof, R.; Brattin, W.; Goldade, M., Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environmental Science & Technology* 1999, 33, (21), 3697-3705.

- Saby, N.; Arrouays, D.; Boulonne, L.; Jolivet, C.; Pochot, A., Geostatistical assessment of Pb in soil around Paris, France. *The Science of the Total Environment* 2006, 367, (1), 212.
- Sauve, S.; Martinez, C.; McBride, M.; Hendershot, W., Adsorption of free lead (Pb²⁺) by pedogenic oxides, ferrihydrite, and leaf compost. *Soil Science Society of America Journal* 2000, 64, (2), 595-599.
- Scheckel, K. G.; Diamond, G. L.; Burgess, M. F.; Klotzbach, J. M.; Maddaloni, M.; Miller, B. W.; Partridge, C. R.; Serda, S. M., Amending soils with phosphate as means to mitigate soil lead hazard: A critical review of the state of the science. *Journal of Toxicology and Environmental Health, Part B* 2013, 16, (6), 337-380.
- Scheckel, K.; Ryan, J., Spectroscopic Speciation and Quantification of Lead in Phosphate-Amended Soils. *Journal of Environmental Quality* 2004, 33, (4), 1288-95.
- Schroth, A.; Bostick, B.; Kaste, J.; Friedland, A., Lead Sequestration and Species Redistribution During Soil Organic Matter Decomposition. *Environmental Science & Technology* 2008, 42, (10), 3627.
- Schwab, A. P.; Lewis, K.; Banks, M. K., Lead stabilization by phosphate amendments in soil impacted by paint residue. *Journal of Environmental Science and Health* 2006, 41, (3), 359.
- Schwarz, K.; Pickett, S. T. A.; Lathrop, R. G.; Weathers, K. C.; Pouyat, R. V.; Cadenasso, M. L., The effects of the urban built environment on the spatial distribution of lead in residential soils. *Environmental Pollution* 2012, 163, 32-39.
- Semlali, R. M.; van Oort, F.; Denaix, L.; Loubet, M., Estimating distributions of endogenous and exogenous Pb in soils by using Pb isotopic ratios. *Environmental Science & Technology* 2001, 35, (21), 4180.
- Serrano, S.; O'day, P. A.; Vlassopoulos, D.; García-González, M. T.; Garrido, F., A surface complexation and ion exchange model of Pb and Cd competitive sorption on natural soils. *Geochimica et Cosmochimica Acta* 2009, 73, (3), 543-558.
- Settle, D. M.; Patterson, C. C., Lead in albacore: guide to lead pollution in Americans. *Science* 1980, 207, 1167.
- Shahid, M., Assessment of lead speciation by organic ligands using speciation models. *Chemical Speciation and Bioavailability* 2012, 24, (4), 248-252.
- Shahid, M.; Pinelli, E.; Dumat, C., Review of Pb availability and toxicity to plants in relation with metal speciation; role of synthetic and natural organic ligands. *Journal of Hazardous Materials* 2012, 219, 1-12.

- Sipos, P.; Nemeth, T.; Kis, V.; Mohai, I., Sorption of copper, zinc and lead on soil mineral phases. *Chemosphere* 2008, 73, (4), 461-469.
- Smith, E.; Kempson, I.; Juhasz, A.; Weber, J.; Rofe, A.; Gancarz, D.; Naidu, R.; McLaren, R.; Gräe, M., In Vivo-in Vitro and XANES Spectroscopy Assessments of Lead Bioavailability in Contaminated Periurban Soils. *Environmental Science & Technology* 2011, 45, (14), 6145.
- Steffen, W., Welcome to the Anthropocene. *Australasian Science* 2016, 37, (2), 28-29.
- Strawn, D. G.; Sparks, D. L., Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. *Soil Science Society of America Journal* 2000, 64, (1), 144-156.
- Su, X.; Zhu, J.; Fu, Q.; Zuo, J.; Liu, Y.; Hu, H., Immobilization of lead in anthropogenic contaminated soils using phosphates with/without oxalic acid. *Journal of Environmental Sciences* 2015, 28, 64-73.
- Tandy, S.; Healey, J. R.; Nason, M. A.; Williamson, J. C.; Jones, D. L., Remediation of metal polluted mine soil with compost: Co- composting versus incorporation. *Environmental Pollution* 2009, 157, (2), 690-697.
- Taylor, M. P.; Camenzuli, D.; Kristensen, L.; Forbes, M.; Zahran, S., Environmental lead exposure risks associated with children's outdoor playgrounds. *Environmental Pollution* 2013, 178, 447-454.
- Tessier, A.; Fortin, D.; Belzile, N.; Devitre, R. R.; Leppard, G. G., Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: Narrowing the gap between field and laboratory measurements. *Geochimica et Cosmochimica Acta* 1996, 60, (3), 387-404.
- Tiberg, C.; Gustafsson, J. P.; Sjostedt, C.; Persson, I., Phosphate effects on copper and lead sorption to ferrihydrite. In London, United Kingdom: Mineralogical Society: London, 2012; Vol. 76, p 2456.
- Traina, S.; Laperche, V., Contaminant bioavailability in soils, sediments, and aquatic environments. *Proceedings of the National Academy of Sciences of the United States of America* 1999, 96, (7), 3365-3371.
- Trivedi, P.; Dyer, J.; Sparks, D., Lead sorption onto ferrihydrite. 1. A macroscopic and spectroscopic assessment. *Environmental Science & Technology* 2003, 37, (5), 908-914.
- Uchimiya, M.; Lima, I. M.; Thomas Klasson, K.; Chang, S.; Wartelle, L. H.; Rodgers, J. E., Immobilization of Heavy Metal Ions (Cu II , Cd II , Ni II , and Pb II) by Broiler Litter-Derived Biochars in Water and Soil. *J. Agric. Food Chem.* 2010, 58, (9), 5538-5544.

- USGS, The National Geochemical Survey - database and documentation: U.S. Geological Survey Open-File Report 2004-1001. U.S. Geological Survey: Reston, VA, 2004.
- Vantelon, D.; Lanzirotti, A.; Scheinost, A.; Kretzschmar, R., Spatial Distribution and Speciation of Lead around Corroding Bullets in a Shooting Range Soil Studied by Micro-X-ray Fluorescence and Absorption Spectroscopy. *Environmental Science & Technology* 2005, 39, (13), 4808-4815.
- Vermeer, A. W. P.; Koopal, L. K., Charge Adjustments upon Adsorption of a Weak Polyelectrolyte to a Mineral Oxide: The Hematite-Humic Acid System. *Journal of Colloid And Interface Science* 1999, 212, (1), 176-185.
- Vidal, M.; Santos, M. J.; Abrão, T.; Rodríguez, J.; Rigol, A., Modeling competitive metal sorption in a mineral soil. *Geoderma* 2009, 149, (3), 189-198.
- Von Lindern, I.; Spalinger, S.; Petroysan, V.; Von Braun, M., Assessing remedial effectiveness through the blood lead : soil/ dust lead relationship at the Bunker Hill Superfund Site in the Silver Valley of Idaho. *Science Of the Total Environment* 2003, 303, (1-2), 139-170.
- Walraven, N.; Bakker, M.; van Os, B. J. H.; Klaver, G. T.; Middelburg, J. J.; Davies, G. R., Factors controlling the oral bioaccessibility of anthropogenic Pb in polluted soils. *Science of the Total Environment* 2015, 506-507, 149-163.
- Walraven, N.; Bakker, M.; van Os, B.; Klaver, G.; Middelburg, J.; Davies, G., Pollution and Oral Bioaccessibility of Pb in Soils of Villages and Cities with a Long Habitation History. *International Journal of Environmental Research and Public Health* 2016, 13, (2), 1-23.
- White, P. D.; Marcus, A. H., The Conceptual Structure of the Integrated Exposure Uptake Biokinetic Model for Lead in Children. *Environmental Health Perspectives* 1998, 106, 1513-1530.
- Wright, S.; Fuller, S.; Jones, S.; McKinney, A.; Rupard, S.; Shaw, S. D. Surficial Geologic Map of the Burlington, Vermont 7.5 Minute Quadrangle; Department of Environmental Conservation: Waterbury, Vermont, 2009.
- Wu, J.; Edwards, R.; He, X. E.; Liu, Z.; Kleinman, M., Spatial analysis of bioavailable soil lead concentrations in Los Angeles, California. *Environmental Research* 2010, 110, (4), 309.
- Xia, K.; Bleam, W.; Helmke, P. A., Studies of the nature of Cu²⁺ and Pb²⁺ binding sites in soil humic substances using x-ray absorption spectroscopy. *Geochimica et Cosmochimica Acta* 1997, 61, (11), 2211-2221.

- Xie, T.; Reddy, K.; Wang, C.; Yargicoglu, E.; Spokas, K., Characteristics and Applications of Biochar for Environmental Remediation: A Review. *Critical Reviews in Environmental Science and Technology* 2015, 45, (9), 939-939.
- Yoon, J. K.; Cao, X.; Ma, L. Q., Application Methods Affect Phosphorus-Induced Lead Immobilization from a Contaminated Soil. *Journal of Environmental Quality* 2007, 36, (2), 373-378.
- Zheng, J.; Huynh, T.; Gasparon, M.; Ng, J.; Noller, B., Human health risk assessment of lead from mining activities at semi-arid locations in the context of total lead exposure. *Environmental Science and Pollution Research International* 2013, 20, (12), 8404.

CHAPTER 2: Geospatial Evaluation of Lead Bioaccessibility and Distribution for Site Specific Prediction of Threshold Limits

Submitted to *Environmental Pollution* (in review).

Jennifer A. Bower¹, Sydney Lister¹, Garrett Hazebrouck¹, Nicolas Perdrial^{1*}

Abstract

Recent work identified the need for site-specific Pb bioaccessibility evaluation and scaled contaminant modeling. Pb heterogeneity has made bioaccessibility characterization difficult, and complicated distribution models. We propose a method for conducting risk-based, multiscale assessment within an area comprised of a single soil and unified Pb impact using field testing, bioaccessibility measurement, EPA Integrated Exposure Uptake and Biokinetic (IEUBK) modeling, and geospatial techniques. This method was applied in Burlington, VT, within an area comprised primarily of a single soil type and high Pb burden (maximum sampled value >15,000 mg kg⁻¹) derived primarily from paint, with nearly half of the housing stock constructed prior to 1950. After analyzing local soil samples for total and bioaccessible Pb, it was determined that bioaccessible and total Pb were well correlated in this area, through which an average bioaccessibility parameter was derived that approximates Pb bioaccessibility for this soil type and Pb impact. This parameter was then used with the IEUBK to recommend the local limit for residential soil Pb be reduced from 400 to 360 mg kg⁻¹, taking into consideration the lowering of the blood lead level threshold for Pb poisoning from 10 to 5 µg dL⁻¹ by the CDC. Geospatial investigation incorporated samples collected during this investigation, as well as samples from a high school summer science academy, and relied on three techniques, used at different scales: kriging of total and background Pb alone, kriging of total and background Pb with housing age as a well-sampled, well-correlated secondary variable (cokriging), and inverse distance weighting (IDW) of total and bioaccessible Pb. Modeling at different scales allowed for characterization of Pb impact at single sites as well as citywide. Model maps show positive correlation between areas of older housing and areas of high

¹ University of Vermont, Department of Geology, Burlington, VT, 05405-1758

Pb burden, as well as potential at different scales for reducing effects of Pb heterogeneity.

Capsule: When used in combination, the employment of site-specific geospatial models and predictive bioaccessibility measurement techniques in an area comprised of a single soil type represents a refinement of currently existing soil Pb assessment procedures.

Keywords: Lead, bioaccessibility, contaminant modeling

2.1. Introduction

Since pre-industrial times, Pb has been used within commercial and residential products, resulting in surficial enrichment worldwide and establishing it as a primary marker of the Anthropocene (Marx et al., 2016). During the 20th century, Pb was ubiquitous, appearing within the solder used on cans of food as well as within gasoline and paint, with 5-6 million metric tons of Pb used within gasoline alone (Laidlaw and Filippelli, 2008). Pb was banned in most products in 1978, with tetraethyl Pb phased out gradually until the early 1990s, although the current use of Pb within aviation fuel and ammunition stand as notable exceptions (Jacobs et al., 2002). Consequent to these massive inputs, Pb is found in soil, in house dust, and is even detected in remote mountain catchments (Davis and Burns, 1999; Kaste et al., 2006), where it persists today. Strong binding to mineralogical and organic soil components gives Pb a long residence time, which is largely controlled by organic matter turnover (Kaste et al., 2006). Mobilization of soil Pb in many cities possesses a seasonal component, with atmospheric Pb spiking during dry months, corresponding to increases in suspended soil particles within the upper atmosphere (Laidlaw and Filippelli, 2008). Pb is a persistent neurotoxin, and sustained contact poses acute developmental risk to children and toxicity and fertility risks to adults (ATSDR, 2007). Soil and seasonal dust Pb sources constitute the main pathway of transmission to children (Walraven et al., 2015), to the extent that they may partially account for the effects of other sources of exposure, such as in the case of the widely-publicized Flint water crisis (Laidlaw et al., 2016). Pb contamination is concentrated in urban centers, where contributions overlap and residents are most vulnerable to legacy pollutants, due in part to historical patterns of

suburbanization and deindustrialization (McClintock, 2015). Pb bioavailability can vary widely according to speciation, soil characteristics, and across sites affected by different Pb sources (Davis et al., 1993; Hettiarachchi and Pierzynski, 2004; Ruby et al., 1999), frustrating attempts at creating a unified bioavailability model across different soil types (Zhu et al., 2016). This indicates that the establishment of a single threshold for Pb contamination in soils is arbitrary and impossible (Henry et al., 2015; Palmer et al., 2015), as it may overestimate or underestimate bioavailability. Instead, bioavailability and distribution of soil Pb may be locally investigated and assessed for the establishment of an individualized Pb contamination threshold, a method that can inform land use practices and aid in the assessment of lead hazard citywide.

Pb possesses a high residence time in soils, where it is tightly held by functional groups on soil organic matter in most natural environments (Kaste et al., 2006; Schroth et al., 2008). This strong binding results from the high electronegativity of Pb, enabling it to bind covalently to oxygen atoms on sorbents (Kaste, 2003). Pb behavior in soils is complex, with metal reactivity and fate governed by soil properties, equilibrium reactions and biogeochemical processes. These factors affect whether Pb occurs as a free hydrated ion, within inner-sphere complexes with mineral surfaces, complexed with organic matter functional groups, or coprecipitated with inorganic molecules (Reeder et al., 2006). Each of these Pb species possesses varying solubility and reactivity, which, along with particle size and availability of reactive sites, dictate the extent to which soil Pb is bioavailable (Traina and Laperche, 1999). Pb carbonates, oxides and hydroxides possess increased solubility relative to Pb phosphates, which are considerably less mobile. Extraction-based *in vitro* procedures can artificially measure

Pb bioaccessibility, which can then be used to derive relative bioavailability to estimate Pb bioavailability in natural systems (Drexler and Brattin, 2007; Ruby et al., 1999). Relative bioavailability of Pb within soil has been determined for areas impacted by smelting operations and mining activity, but is understudied for soils affected by Pb paint *in situ*.

Mielke and others (Laidlaw et al., 2016; Mielke et al., 2013) established a spatial correlation between Pb in city centers and elevated blood Pb levels (BLL). Through the work of a high-school science program and exploratory XRF field testing, it was determined that Burlington possesses high soil Pb due to a high proportion of older housing containing historical Pb paint. Therefore, this study chose to target areas of highest contamination by sampling soil adjacent to painted structures, using this data in conjunction with samples collected away from structures. Using this data, Pb concentration can be estimated at unsampled sites through interpolative geospatial and geostatistical models, including kriging, cokriging, and inverse distance weighing (IDW) (Cattle et al., 2002; Stewart et al., 2014). Schwarz et al. (2012), identified the importance of scale in modeling Pb distribution, as larger Pb particles from structures tend to be localized, resulting in elevated soil Pb adjacent to structures, while background levels tend to be lower and comprised of finer particles. Such contrast between spatially delimited influences points to the need for incorporating different modeling scales, which we have expanded to include different modeling techniques, to analyze distribution of Pb from the scale of a city to the scale of a single residence. Kriging, a general term used to describe a range of least-squares regression algorithms, is used to evaluate the distribution of a given attribute in unsampled areas by averaging

measured values in the same neighborhood (Goovaerts, 1999). If data is highly skewed, as can occur when an attribute has a low background level but wide range of values, transformations are appropriate before subjecting the data to modeling (Wu et al., 2006). When existing data is not comprehensive enough to form an accurate prediction, a well-correlated, comprehensively sampled secondary variable may be added to improve the estimation of the model, a technique known as cokriging. Like kriging, inverse distance weighting is built on the assumption that an attribute at a single location is a weighted average of local known data points, with the difference that in IDW, closer data points are given greater weight than data points farther away (Goovaerts, 1999; Robinson and Metternicht, 2006).

With the help of these methods, remediation efforts can be expanded from areas with high reported BLLs and high Pb in soil and dust to include areas of high predicted BLLs and soil Pb identified by modeling. Bioaccessibility parameters and Pb concentration in soil, dust, and water can then be used to extrapolate the expected burden of Pb to children using predictive biokinetic modeling (Laidlaw and Taylor, 2011; Stewart et al., 2014; White and Marcus, 1998). The principle goal of this study is to establish a framework for constraining the extent and relative bioavailability of soil Pb in a city with a high concentration of old housing stock (Burlington, VT), to be used in investigating implications for safe soil Pb thresholds and modeling Pb distribution within areas of high risk. Once Pb bioavailability and distribution are constrained for the area, this data may be used to estimate risk to humans citywide using predictive blood lead level modeling and geostatistical interpolation techniques (Moukana et al., 2013), for use in future preventive health efforts and site remediation.

2.2. Materials and Methods

2.2.1. Study location

The city of Burlington, VT was chosen as a study site, with over 47% of houses built prior to 1950, most consisting of painted wood. Burlington soils are comprised of a single soil type, the Windsor loamy sand, comprised of glaciofluvial sediment. A local Housing and Urban Development (HUD) funded program, the Burlington Lead Program (BLP), part of the City of Burlington Community and Economic Development Office, provides lead hazard outreach and abatement assistance to the community in the form of soil barriers and window replacement, and serves as a community partner in this investigation. According to available data from the BLP (data.burlingtonvt.gov), the mean construction date of houses that have been chosen for remediation is 1906 ($n = 325$), suggesting paint is an important local contributor of Pb. The Old North End and South End neighborhoods contain the highest concentration of sites that have received window and soil barrier remediation treatments from the BLP (SI Figure 1). Though paint is considered the principal source of Pb within this area, the possibility of minor tetraethyl lead (TEL) contributions from pre-catalytic gasoline should be acknowledged. Research has suggested that wind currents deposited particulate TEL on structures, where it was subsequently washed into the surrounding soil, indicating that soil adjacent to exterior walls on high-traffic roadways may contain multiple sources of Pb (Mielke et al., 2011). For modeling purposes, and given Burlington's history of low traffic density, we have chosen to focus on the relationship between older housing and Pb, but measurements may reflect more than one source.

2.2.2. Sample collection and preparation

One hundred and one soil samples were collected between 0 and 10 cm at 9 public and residential sites in and around Burlington, Vermont during the summer and fall months of 2015 and spring months of 2016. Sample locations are given in Figure 2a and 2b. Residential sites were sampled with permission. Samples were augured from within 0.5 m of building exteriors, from all accessible sides, with control samples taken at least 2 m away from buildings at each site. If mulch or grass was present, sample was obtained from soil underlying groundcover. After sampling, visible organic material was separated and saved, samples were dry sieved through 2 mm mesh, and a fraction was ball-milled for 7 minutes using a steel ball mill.

2.2.3. Total soil Pb analysis

A fraction of the powderized fraction was packed into XRF canisters and subjected to x-ray fluorescence (XRF) spectroscopy for 60 seconds, in duplicate, using a Niton XL3t XRF analyzer to obtain bulk Pb concentrations. Results were enforced for accuracy by regularly analyzing the standard NIST-2780, and triplicates were averaged, with any results lower than the detection limit ($\sim 7.5 \text{ mg kg}^{-1}$) assumed negligible (0) for the purposes of modeling and computation.

2.2.4. Bioaccessible Pb analysis

To assess Pb bioaccessibility, 95 samples were subjected to glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) extraction following the EPA method 1340 (EPA, 2013). One gram ($\pm 0.05 \text{ g}$) of each sieved fraction of soil was suspended in $100 \pm 0.5 \text{ mL}$ of 0.4 M glycine solution, adjusted to pH 1.5 using ultrapure HCl, heated to $37 \pm 2 \text{ }^\circ\text{C}$ and shaken at 300 rpm for an hour within a BioMaker BS-ES-60 incubator orbital shaker. After digestion,

40 mL of solution was extracted with a syringe and filtered through a 0.45 μm GHP filter. Following dilution with 1% ultrapure HNO_3 , the amount of extracted Pb was analyzed using a Jobin Yvon Horiba ICP-OES with mono line at 220.353 nm and a standard curve ranging from 0.5 to 10.0 mg L^{-1} . Acidified glycine solution blanks were analyzed periodically between samples. *In vitro* bioaccessible (IVBA) Pb was calculated using the equation for IVBA given in EPA method 1340. This parameter was subsequently used to calculate the relative *in vivo* bioavailability (RBA) using a weighted linear regression (EPA, 2013). RBA values may be slightly overestimated, given that Pb phosphates can dissolve at the specified pH that would otherwise remain stable in certain *in vivo* conditions (Obrycki et al., 2016).

2.2.5. Predictive blood Pb level modeling

To predict blood Pb levels for measured soils, the EPA's Integrated Exposure Uptake Biokinetic (IEUBK) model was run for each sample (White and Marcus, 1998). Within each model iteration, total Pb concentration from XRF analysis was submitted as the soil Pb parameter, and the average RBA proportion derived from the slope of the data regression analysis was divided in half as per IEUBK protocol to reflect measured absorption within humans, then used as the absolute bioavailability parameter. "Absolute bioavailability" is defined as the amount of Pb entering the blood through exposure pathways divided by the total substance ingested. This parameter was calculated using the EPA's assumption that soluble lead is estimated to have 50 percent absolute bioavailability within humans, an estimate that was validated during the construction of the IEUBK through validation with *in vivo* study results (EPA, 1999). All non-soil Pb sources were left at default parameters, and corresponding household

dust burden estimated using a multiple source average. This model was also used to estimate a threshold for contaminated soil by reverse-modeling the minimum total soil Pb needed to achieve the EPA's action limit for Pb BLLs in children, $5 \mu\text{g dL}^{-1}$ (CDC, 2012) using the absolute bioavailability parameter.

2.2.6. Geospatial analysis and modeling

Lead paint was banned for use in housing in 1978 (CDC 2013) within the United States, so structures built after 1978 are considered uncontaminated for the purposes of this study. Positive correlation has been observed between age of housing and elevated blood lead levels (BLLs) within children (Kim et al., 2002), which likely correlates with the number of lead paint coats applied since each structure's inception and Pb dust accumulation time in soils. To identify properties with the greatest lead risk, parcel data from the towns of Burlington, South Burlington, and Winooski was spatially joined to housing age point information from the Chittenden County Regional Planning Commission within ArcGIS to display relative housing ages within the study area (SI Figure 2). Both datasets were accessed from the website of the Vermont Center for Geographic Data (<http://vcgi.vermont.gov/>). This parcel join layer was used in conjunction with total Pb concentration data, consisting of data from this study merged with total Pb data collected by high school student participants at the Governor's Institute of Vermont (GIV 2014, 2015, 2016), and building footprints obtained from OpenStreetMaps, a crowdsourced web repository of structure and road data. Soil samples from GIV were analyzed using the XRF instrument referenced above, without duplication, and were collected from publicly accessible spaces, such as road verges, parks, and University of Vermont buildings.

Total Pb values obtained from this study and GIV sampling were used in conjunction with housing age parcel layer to construct two exploratory predictive distribution maps using ordinary kriging and cokriging within the ArcGIS Geostatistical Wizard. For the total Pb distribution models, samples below the XRF detection limit ($\sim 7.5 \text{ mg kg}^{-1}$) and higher than $10,000 \text{ mg kg}^{-1}$ were excluded, remaining samples log transformed, and detrended using a polynomial approach. Within kriging model, total Pb parameter was set to covariance and optimized using Geostatistical Wizard; in cokriging model total Pb was set to covariance, housing age set to semivariogram, and optimized using Geostatistical Wizard. Background Pb distribution models were constructed using samples greater than 2 m from OpenStreetMaps-derived residential building footprints, which were considered background levels for the purposes of this study, with lognormal adjustment and constant polynomial kernel trend removal also performed to account for the spread in values and minimize the skewing effect of dense sample groups. Models were set to best fit using procedure detailed in total Pb model description above. At the scale of single sites, IDW was used instead of kriging for its simplicity, as well as for the higher weight given to close sites during interpolation. Total Pb and RBA values were mapped at a local scale using inverse distance weighting (IDW) at a power of 1.5, with building footprints removed, to model spatial heterogeneity at single residences. Within all map figures in the following sections, city limits are delimited by black lines and labeled in all capitals; approximate neighborhood areas are indicated in mixed case.

2.3. Results

2.3.1. Total Pb distribution

Mean, median, and range values of total Pb are given in Table 1 for residential project (non-GIV) samples. Measurements are divided by structure-adjacent samples ($n = 69$), located within 0.5 m of structures, and site controls ($n = 8$), sampled at least 2 m away from structures. Samples from non-residential locations (e.g. public parks) were excluded from these statistics. Mean year of construction for structures sampled is 1895. Thirty-nine (39) percent of samples close to structures exceed the EPA guidance limit for soil Pb in non-play areas, i.e. 1200 mg kg^{-1} . Eighty-four (84) percent of samples close to structures and 38% of site controls exceed the EPA guidance limit for soil Pb in residential play areas, 400 mg kg^{-1} . The maximum concentration measured is approximately 44 times this threshold. Control maximum is over double this threshold, possibly because a paint chip or a historical source location was overlooked when selecting this control site. With high maximum control value removed, mean of controls would be 230 mg kg^{-1} . One hundred (100) percent of residential sites sampled contained one or more samples exceeding 400 mg kg^{-1} ; 89% of sites contained one or more samples exceeding 1200 mg kg^{-1} . Sixty-three (63) percent of sites possessed a structure-adjacent sample lower than 400 mg kg^{-1} .

2.3.2. Measured and predicted bioaccessibility

A linear fit of bioaccessible vs. total Pb displays an r^2 of 0.96 when forced to origin (Figure 1). At lower Pb concentrations ($<100 \text{ mg kg}^{-1}$), RBA measurements may be overestimated, with extractable Pb values near the limit of detection ($\sim 7.5 \text{ mg kg}^{-1}$). An overall estimate of Pb bioaccessibility within this sample area is represented by the

slope of the regression (0.49), lower than the EPA's estimated bioaccessibility IEUBK parameter of 0.60. This implies that 49% of total soil Pb in this study area is bioaccessible.

The results of IEUBK modeling give a greater predicted absorption among young toddlers than infants and older children (reflecting the higher absorption capacity of younger children), and a predicted BLL maximum far exceeding the recently lowered CDC threshold, $5 \mu\text{g dL}^{-1}$, at $79.7 \mu\text{g dL}^{-1}$ (CDC, 2012). The mean and median BLLs for all included age ranges are $12.68 \mu\text{g dL}^{-1}$ and $8.85 \mu\text{g dL}^{-1}$, respectively. Reverse modeling to estimate a contaminated soil Pb action level for the study area based on the CDC limit of $5 \mu\text{g dL}^{-1}$ yielded a value of 360 mg kg^{-1} , lower than the EPA's soil threshold of 400 mg kg^{-1} . This is in spite of the EPA's higher default bioaccessibility parameter, 0.60, because the EPA's soil threshold has not been updated to match the CDC's revised BLL threshold (Young, 2013). This finding was confirmed by modeling a hypothetical soil exposure just below the action level, 399, and receiving a BLL prediction for the most susceptible age range (1-2 years) of $5.7 \mu\text{g dL}^{-1}$.

2.3.3. Pb geolocation and techniques for multiscale distribution modeling

In an effort to geolocate areas likely to contain high levels of soil Pb, preliminary efforts were made to visualize the distribution of older residential parcels in Burlington. Residential areas where older housing is concentrated include the "Old North End" and "South End" neighborhoods of Burlington, and Winooski, an neighboring town. Distribution of total Pb mirrors this trend, with the highest concentrations of Pb located in neighborhoods with older residential structures (Figure 2a). Pb distribution away from structures (background) similarly reflects the general distribution of structure age,

with values systematically below 100 mg kg^{-1} in the northern part of the city (the “New North End” neighborhood), a residential area developed in the last 50 years (Figure 2b). In historic neighborhoods, where older housing stock is concentrated (the Old North End and South End neighborhoods), background values are variable and sometimes exceed 335 mg kg^{-1} , a tenfold increase from the countywide background value of 27.1 mg kg^{-1} ($\pm 3.6 \text{ mg kg}$) obtained by the National Geochemical Survey (USGS, 2004). Using total Pb soil analyses and housing ages as first order variables, we generated a predictive map of total Pb concentration in topsoils over the entire study area using a kriging analysis (Figure 2c). This model yields a prediction error mean of 26.1, giving the average difference between measured and predicted values, root mean square (RMS) of 707.8, and root mean square standardized (RMSS) of 16.4. Positive prediction error mean indicates Pb concentration was slightly overestimated; since data was highly scattered, root mean square is high, but lower than average standard error (ASE), indicating model generally underestimated variability of data. When cokriging was performed, incorporating densely sampled, well-correlated housing age points, RMS increased slightly and RMSS decreased (prediction error mean = -66.8; RMS = 733.8; RMSS = 3.7; ASE = 689.0); low RMSS and correspondence between RMS and ASE suggest model predicts data variability well, though actual concentrations are generally underestimated. High RMS values indicate total Pb concentration is highly variable within this area and difficult to model, an expected result given initial field characterization. Incorporation of housing age did not significantly change prediction accuracy, although it generally improved the model’s ability to predict the variability of the data. Areas of predicted high Pb concentration are distributed in neighborhoods

such as the Old North End, South End, and Winooski areas. The southern part of the University of Vermont, Redstone Campus, is predicted to give high values due to high measured concentrations within GIV samples; Trinity Campus, within Burlington but near the southern border of Winooski, containing old University-owned painted housing, also displays high predicted values. Constant polynomial kernel trend removal constrained fit to discrete areas, rather than the total map. Areas of low sampling resolution or homogeneous concentration are monochromatic, while areas with a range of concentrations, usually corresponding to high sampling density, display greater color variation. Pb measurements that were geolocated 2 m or greater distance from Open Street Maps-defined structure perimeters were considered background levels, and ordinary kriging and cokriging analyses were performed upon this data in the same manner, with other Pb measurements excluded from the model. Kriging model resulted in a prediction error mean of -18.1, RMSS of 0.8, and RMS of 356.9, while background cokriging model (Figure 2d) possesses a prediction error mean of -52.6, RMSS of 10.1, and RMS of 351.2, showing that inclusion of housing age data did not significantly improve goodness of fit of model. Negative prediction error mean and positive RMSS indicates model underestimated overall background Pb concentrations and data variability, respectively. Areas with clustered samples, low sampling resolution or where access to structure perimeter was difficult display weaker prediction accuracy as in previous model. Areas of high measured and predicted Pb values within background model roughly coincide with areas of predicted total Pb areas of higher housing age.

The problem of heterogeneity within citywide mapping efforts may be addressed by examining Pb behavior and distribution at the scale of a single structure, a scale that

can also aid in developing site-specific remediation strategies and predicting the local health burden around same-aged housing structures. Within individual residential sites, IDW prediction map with building footprints removed corresponds more strongly to measured values than general kriging map, giving a better local estimation (Figure 3a). Since building footprints are sourced from crowdsourced OpenStreetMaps digitization, and given that photographic collection of orthophoto basemap occurred at an angle, structure extents do not perfectly match aerial photography, but may roughly correspond to foundation extent. IDW site interpolation using total Pb measurements displays considerable variability, with no clearly discernible relationship between total soil Pb and aspect, but some possible influence of overlapping paint inputs contributing to higher Pb between the two houses. Predicted blood lead levels were examined on a site-specific scale, giving the potential health burden of two structures in Figure 3b to children ages 1-2, the most susceptible age group to Pb exposure. Using the CDC BLL threshold of $5 \mu\text{g dL}^{-1}$, and excluding controls, it is determined with the IEUBK that fifteen out of nineteen soils have the potential of exceeding this threshold when ingested by children who interact with soil through normal play behavior at these two properties. With the potential health burden to children exceeding the CDC defined threshold for toxicity at these structures, and assuming an average bioaccessibility, these findings may be extrapolated to other residential structures of similar age within the larger area. Through spatial analysis it was determined that 1,640 residential properties in the city of Burlington are older than 1900, with most constructed near the turn of the century. This implies that 24.8% of sites within the city bear similar concentrations to the structures examined at the site-specific scale, giving a maximum

risk potential to children that exceeds the $5 \mu\text{g dL}^{-1}$ federal definition of Pb poisoning (Figure 4).

2.4. Discussion and Conclusions

Large-scale surveys of soil Pb have been conducted primarily in two ways: grid-based sampling, and exploratory sampling near smelters and other industrial point sources (Markus and McBratney, 2001). This study chose an alternative approach; with local background levels already constrained citywide by summer sampling conducted by high school students (GIV 2014, 2015, 2016), samples for this study were collected from areas abutting structure perimeters, targeting areas of highest probable contamination. The combination of these datasets, with consideration that access was constrained to areas for which permission was granted, produced an irregular sample distribution, but one that incorporated both structure-adjacent and “background” values. This type of sample distribution may more closely correspond with the type of sampling practical for local organizations and governments, given that access to soil is not always possible in a gridded fashion; instead, in areas with older housing, housing age data can provide a good starting point for conducting targeted investigation. Given the spatial heterogeneity of Pb distribution in this city, sampling of soil Pb can produce radically different outcomes depending on the location, culminating in very high Pb concentration near structures, or negligible concentrations further away from structures, reflecting the inherently skewed distribution of lead in paint-impacted areas. To mitigate the effect of such variability, we experimented with including a secondary, well-sampled variable (housing age) within the interpolation model to better estimate Pb concentration in areas with low sample density. Multiple sample collection at each

site gives some estimation of site heterogeneity; half of the sites possessing both a sample exceeding $1,200 \text{ mg kg}^{-1}$ Pb and a sample less than 400 mg kg^{-1} Pb. Mielke, et al. (2011), spearheaded efforts to characterize Pb burdens in cities, faced with rapidly rising levels of Pb from paint and gasoline, and determined that the major contributor within Baltimore was gasoline, extrapolating this finding to other US cities. This assumption was partly based on available data showing that areas of historically high traffic density contained high levels of Pb near brick building exteriors. Such an expectation was not found to hold for Burlington, with its history of low automobile traffic density and high concentration of aged housing stock. In this study, spatial correlations between areas of high soil lead concentration and areas of older housing verifies the hypothesis that the primary source of Pb in this area is paint, a finding that is not uncommon within cities in the northeastern U.S. (EPA, 1998). Our discovery that Pb within this soil has a mean bioaccessibility of 49% supports this conclusion, without ruling out minor contributions from leaded gas. Prior studies have measured bioaccessibility of Pb in paint and paint-generated dust, though none have focused on Pb bioaccessibility in paint-impacted soils. Hunt measured the relative bioavailability of Pb within historical paint samples and paint after artificially mixing paint with soil, deriving fraction values of 37.2-100.0 for paints composed primarily of Pb carbonates (Hunt, 2016). Rasmussen et al. derived a mean fraction value of 75 ± 18 within urban home dust probably contaminated with Pb from paint (Rasmussen et al., 2011). The linear relationship exhibited by bioaccessible and total Pb in this study is indicative of the homogeneity of soil characteristics and Pb speciation within the study area. Interactions between the local soil, derived from glaciofluvial sediment, climate, and Pb

sources are apparently uniform enough that a predicted bioaccessibility parameter may be generated. This implies that individual Pb-impacted communities with a uniform soil type could perform a streamlined version of the approach outlined in this study. For a given area, once a limited number of samples are collected and tested for total and bioaccessible Pb, a mean bioaccessibility parameter can be derived from the slope of the regression, and a site specific Pb threshold determined using the IEUBK model. This simple, comprehensive procedure can help advise and inform city governments, health departments, and community members of the extent to which soil Pb is a local risk, without performing extensive testing or relying on thresholds that haven't been site-tested. The variation exhibited by Pb bioaccessibility at the scale of individual residences (SI Figure 3) suggests that for practical implementation of this procedure, users should weight thresholds to represent a high average. This would minimize the extent to which bioaccessibility is underestimated for samples that positively deviate from the mean bioaccessibility parameter, and conform with a tendency towards conservative estimation of bioaccessibility founded on the understanding that, from a human health perspective, there is no acceptable level of Pb in blood (CDC, 2012). Sources of error within bioaccessibility measurements in this area may derive from deviations in sieving protocol (with 2 mm rather than 0.5 mm mesh) and sampling depth (sampling the first 10 cm rather than the top inch).

Geospatial modeling results indicate that with increasing data accuracy, it is possible to model geochemical distribution and assess risk with increasing resolution at multiple scales. Recent predictive investigations have focused on the kriging method as an estimation of citywide Pb distribution (Ha et al., 2014; Saby et al., 2006; Solt et al.,

2015); fewer studies have incorporated housing age as a variable, used in the past within principle component analysis or general linear model frameworks (Schwarz et al., 2013; Yesilonis et al., 2008). Given that housing age and Pb concentration are strongly correlated in our study area, we expected that using spatially constrained age data (created by linking housing ages with parcel data) as a first-order variable alongside total Pb values within a cokriging model would provide a robust prediction of Pb location in areas with older housing stock. The effect of cokriging with this secondary variable proved almost negligible or worse from a statistical perspective when compared to kriging alone, reflecting the heterogeneity of soil Pb in Burlington and skewing from background measurements. The minor improvement it offered in modeling background Pb, a dataset with a narrower spread and less extreme variation, hints at the future potential of this technique to refine contaminant models in areas with spatially constrained sources, especially if area is undersampled or contaminant distribution is less heterogeneous. Visually, cokriging and kriging prediction maps of total Pb differ somewhat in depiction of hotspot locations, although it would be impossible to call cokriging model an improved representation of soil Pb distribution without groundtruthing in unsampled areas. In general, similarity in spatial distribution of soil Pb within cokriging and kriging maps, as well as similarity between background and total Pb maps, suggests geographic trends in Pb distribution are linked with spatial distribution of older housing.

Overall, neighborhood investigation shows the large potential burden of soil Pb in areas of lower income than surrounding areas of Burlington. The correspondence of elevated background Pb levels with areas of older housing seems to indicate that

background Pb levels have generally increased within all topsoil in these regions, likely due to seasonal mobilization of Pb dust, which tends to occur in dry summer months. Residents in affected areas are less likely to be able to afford the high cost of remediation, and likely have a higher susceptibility to Pb-related health effects than residents in wealthier areas. Despite strict rules governing Pb paint management in rental structures, landlords in the area do not always comply (Despart, 2015). Establishing a geospatial link between the general distribution of housing age data and in-field testing provides a way to comprehensively target residential structures for preventative testing and remediation efforts in this area. By using predictive geospatial techniques to identify areas at risk of Pb contamination, communities can target areas with a high probability of elevated BLLs, and increase testing resolution within these areas.

The low overall goodness-of-fit of cokriging and kriging analyses points to issues with spatial accuracy, the heterogeneity of Pb behavior and distribution within sample sites, and some of the assumptions made during this study. Since paint-sourced Pb decreases with distance from a structure (Clark and Knudsen, 2013), distinguishing between samples close and far from structures depends on the correctness of building footprints, which often deviate significantly from actual structure extents, as the OpenStreetMaps dataset consists of user-drawn polygons, often hastily rendered, is incomplete within some areas of the study and constantly evolving. This introduced error when geospatial buffer tools were used to distinguish background from structure-adjacent samples, as tools determined 90% of samples to be background, though actual proportion is closer to 75%. This misclassification may be partly responsible for the

general underestimation of background Pb within cokriging model. Increased model error in areas of clustered samples, low sample density, and structure-distant samples suggests Pb distribution in this study location is relatively heterogeneous, an effect that is apparent not only within larger dataset, but also within background Pb measurements citywide. Limiting sample set to background measurements increased model prediction accuracy, suggesting impact of heterogeneity on model, while still a factor, was reduced. Parcel data contains polygonal and positional inaccuracy, especially since parcel lines often extend to road centerlines instead of road edges, complicating efforts to study intersecting Pb contributions from paint and gas in this area.

As shown in site-specific analysis, a final hurdle in using general predictive models at a city scale to predict Pb distribution resides within the large range of Pb values citywide. Given the high residence time and low mobility of Pb within soils, it tends to accumulate in discrete “hotspots”. This leads to extreme disparities in Pb concentration, with values over $5,000 \text{ mg kg}^{-1}$ found only meters away from locations with a few hundred mg kg^{-1} . Such heterogeneity emphasizes the importance of collecting multiple samples within sites suspected of being affected by soil Pb. Though data was adjusted using a logarithmic and constant detrending approach, large spread of concentration values combined with clustered nature of samples ensures standard error and RMS are high, an effect that was dampened when structure-adjacent samples were excluded. This is partly a factor of the inability of large-scale models to account for Pb hotspots at the scale needed to make decisions about an individual site. For this reason, citywide kriging and cokriging models are useful as a general rather than a specific prediction tool for estimating Pb concentration, and, if testing is constrained to areas of

probable contamination, tend to represent the maximum burden of soil Pb for a given area. Efforts to geospatially map such varying concentrations will have high error until geolocation accuracy and understanding of Pb distribution heterogeneity improves. Effects of soil Pb heterogeneity on model error might be reduced within future citywide interpolation models by using maximum Pb values of individual sites once a robust bank of samples has been established. Within this investigation, the presence of sample clusters at residential sites increased error when constructing citywide prediction maps, but allowed for mapping Pb on smaller scales, such as a neighborhood or a single structure. Once the spread of values and health burden were constrained at two structures of a certain age, these findings were extrapolated to other houses of a similar age, providing a useful way of predicting potential maximum Pb burden at individual sites despite wide range of values. No one interpolation method can account for both city-scale and site-scale predictive distribution of Pb alone. Rather, spatial analysis methods were used in conjunction with kriging, cokriging and IDW prediction tools to provide insight into Pb behavior at multiple scales.

As an anthropogenic pollutant, Pb is necessarily intertwined with legacies of human development. The success of future efforts to constrain Pb location geospatially requires linking on-the-ground geochemical investigation with historical data regarding point sources such as housing age, traffic intensity, and industrial activities. Though location data is available for sites remediated by the Burlington Lead Program using window replacements, revegetation of bare soil, and barrier placement, historical data concerning the location and completion of soil removal and *in situ* remediation efforts, including paint scraping and/or covering is not currently available. It is in the interest of

researchers and residents to create and maintain such data for the public good, and a recommendation of this study. Results of soil testing data from this study will be made accessible to local public health organizations and city residents through an open data repository.

Acknowledgements

Part of this research was funded by the UVM College of Arts and Sciences small grant program and the UVM geology Hawley-Mudge award. Special thanks to student and faculty participants within the Governor's Institute of Vermont for collecting samples and making data accessible, the Burlington Lead Program for providing guidance and sampling sites, Jarlath O'Neill Dunne for expert GIS instruction, the Vermont Center for Geographic Data for data resources, and OpenStreetMaps for building extents.

2.5. References

- Cattle, J.; McBratney, A. B.; Minasny, B., Kriging method evaluation for assessing the spatial distribution of urban soil lead contamination. *Journal of Environmental Quality* 2002, 31, (5), 1576-1588.
- CDC, Low Level Lead Exposure Harms Children: A Renewed Call for Primary Prevention: Report of the Advisory ommittee on Childhood Lead Poisoning Prevention of the Centers for Disease Control and Prevention. 2012.
- Clark, J. J.; Knudsen, A. C., Extent, characterization, and sources of soil lead contamination in small-urban residential neighborhoods. *Journal of Environmental Quality* 2013, 42, (5), 1498-1506.
- Davis, A. P.; Burns, M., Evaluation of lead concentration in runoff from painted structures. *Water Research* 1999, 33, (13), 2949-2958.
- Davis, A.; Drexler, J.; Ruby, M.; Nicholson, A., Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. *Environmental Science & Technology* 1993, 27, (7), 1415.
- Despart, Z., Burlington considers prosecuting landlord. *Burlington Free Press* 2015.
- Drexler, J.; Brattin, W., An In Vitro Procedure for Estimation of Lead Relative Bioavailability: With Validation. *Human and Ecological Risk Assessment* 2007, 13, (2), 383-401.
- EPA, IEUBK Model Bioavailability Variable (Short Sheet) 1999.
- EPA, In Vitro Bioaccessibility Assay for Lead in Soil. SW-846 2013, (1340), 24.
- EPA, Sources of Lead in Soil: A Literature Review, EPA 747-R-98-001a. National Center for Environmental Assessment, US Environmental Protection Agency, Washington, D.C. 1998.
- Goovaerts, P., Geostatistics in soil science: state-of-the-art and perspectives. *Geoderma* 1999, 89, (1), 1-45.
- Ha, H.; Olson, J.; Bian, L.; Rogerson, P., Analysis of Heavy Metal Sources in Soil Using Kriging Interpolation on Principal Components. *Environmental Science & Technology* 2014, 48, (9), 4999.
- Henry, H.; Naujokas, M.; Attanayake, C.; Basta, N.; Cheng, Z.; Hettiarachchi, G.; Maddaloni, M.; Schadt, C.; Scheckel, K., Bioavailability-Based In Situ Remediation To Meet Future Lead (Pb) Standards in Urban Soils and Gardens. *Environmental Science & Technology* 2015, 49, (15), 8948.

- Hettiarachchi, G. M.; Pierzynski, G. M., Soil lead bioavailability and in situ remediation of lead- contaminated soils: A review. *Environmental Progress* 2004, 23, (1), 78-93.
- Hunt, A., Relative bioaccessibility of Pb-based paint in soil. *Environmental Geochemistry and Health* 2016, 38, (4), 1037.
- Jacobs, D. E.; Clickner, R. P.; Zhou, J. Y.; Viet, S. M.; Marker, D. A.; Rogers, J. W.; Zeldin, D. C.; Broene, P.; Friedman, W., The prevalence of lead-based paint hazards in U.S. housing. *Environmental Health Perspectives* 2002, 110, (10), A599.
- Kaste, J., Tracing the retention and redistribution of lead and other atmospheric fallout in soils. In Friedland, A. J., Ed. ProQuest Dissertations Publishing: 2003.
- Kaste, J.; Bostick, B.; Friedland, A.; Schroth, A.; Siccama, T., Fate and Speciation of Gasoline- Derived Lead in Organic Horizons of the Northeastern USA. *Soil Science Society of America Journal* 2006, 70, (5), 1688-1698.
- Kim, D.; Staley, F.; Curtis, G.; Buchanan, S., Relation between housing age, housing value, and childhood blood lead levels in children in Jefferson County, Ky. *American Journal of Public Health* 2002, 92, (5), 769-72.
- Laidlaw, M. A. S.; Filippelli, G. M., Resuspension of urban soils as a persistent source of lead poisoning in children: A review and new directions. *Applied Geochemistry* 2008, 23, (8), 2021-2039.
- Laidlaw, M. A. S.; Taylor, M. P., Potential for childhood lead poisoning in the inner cities of Australia due to exposure to lead in soil dust. *Environmental Pollution* 2011, 159, (1), 1-9.
- Laidlaw, M.; Filippelli, G.; Sadler, R.; Gonzales, C.; Ball, A.; Mielke, H., Children's Blood Lead Seasonality in Flint, Michigan (USA), and Soil-Sourced Lead Hazard Risks. *International Journal of Environmental Research and Public Health* 2016, 13, (4), 1-13.
- Markus, J.; McBratney, A. B., A review of the contamination of soil with lead. *Environment International* 2001, 27, (5), 399-411.
- Marx, S. K.; Rashid, S.; Stromsoe, N., Global-scale patterns in anthropogenic Pb contamination reconstructed from natural archives. *Environmental Pollution* 2016, 213, 283-298.
- McClintock, N., A critical physical geography of urban soil contamination. *Geoforum* 2015, 65, 69-85.

- Mielke, H.; Gonzales, C. R.; Mielke, P., The continuing impact of lead dust on children's blood lead: Comparison of public and private properties in New Orleans. *Environmental Research* 2011, 111, (8), 1164-1172.
- Mielke, H.; Gonzales, C. R.; Powell, E.; Mielke, P., Environmental and health disparities in residential communities of New Orleans: The need for soil lead intervention to advance primary prevention. *Environment International* 2013, 51, 73-81.
- Moukana, J.; Asaue, H.; Koike, K., Co-kriging for modeling shallow groundwater level changes in consideration of land use/land cover pattern. *Environmental Earth Sciences* 2013, 70, (4), 1495-1506.
- Obrycki, J. F.; Basta, N. T.; Scheckel, K.; Stevens, B. N.; Minca, K. K., Phosphorus Amendment Efficacy for In Situ Remediation of Soil Lead Depends on the Bioaccessible Method. *Journal of Environmental Quality* 2016, 45, (1), 37.
- Palmer, S.; McIlwaine, R.; Ofterdinger, U.; Cox, S. F.; McKinley, J. M.; Doherty, R.; Wragg, J.; Cave, M., The effects of lead sources on oral bioaccessibility in soil and implications for contaminated land risk management. *Environmental Pollution* 2015, 198, 161-171.
- Rasmussen, P.; Beauchemin, S.; Chénier, M.; Levesque, C.; Maclean, L.; Marro, L.; Jones-Otazo, H.; Petrovic, S.; McDonald, L.; Gardner, H., Canadian House Dust Study: Lead Bioaccessibility and Speciation. *Environmental Science & Technology* 2011, 45, (11), 4959.
- Reeder, R. J.; Schoonen, M. A. A.; Lanzirotti, A., Metal speciation and its role in bioaccessibility and bioavailability. *Reviews in Mineralogy and Geochemistry* 2006, 64, 59-113.
- Robinson, T. P.; Metternicht, G., Testing the performance of spatial interpolation techniques for mapping soil properties. *Computers and Electronics in Agriculture* 2006, 50, (2), 97-108.
- Ruby, M.; Schoof, R.; Brattin, W.; Goldade, M., Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environmental Science & Technology* 1999, 33, (21), 3697-3705.
- Saby, N.; Arrouays, D.; Boulonne, L.; Jolivet, C.; Pochot, A., Geostatistical assessment of Pb in soil around Paris, France. *The Science of the Total Environment* 2006, 367, (1), 212.
- Schroth, A.; Bostick, B.; Kaste, J.; Friedland, A., Lead Sequestration and Species Redistribution During Soil Organic Matter Decomposition. *Environmental Science & Technology* 2008, 42, (10), 3627.

- Schwarz, K.; Weathers, K.; Pickett, S.; Lathrop, R.; Pouyat, R.; Cadenasso, M., A comparison of three empirically based, spatially explicit predictive models of residential soil Pb concentrations in Baltimore, Maryland, USA: understanding the variability within cities. *Environmental Geochemistry and Health* 2013, 35, (4), 495-510.
- Solt, M.; Deocampo, D.; Norris, M., Spatial Distribution of Lead in Sacramento, California, USA. *International Journal of Environmental Research and Public Health* 2015, 12, (3), 3174-3187.
- Stewart, L.; Farver, Jr.; Gorsevski, P.; Miner, J., Spatial prediction of blood lead levels in children in Toledo, OH using fuzzy sets and the site-specific IEUBK model. *Applied Geochemistry* 2014, 45, 120-129.
- Traina, S.; Laperche, V., Contaminant bioavailability in soils, sediments, and aquatic environments. *Proceedings of the National Academy of Sciences of the United States of America* 1999, 96, (7), 3365-3371.
- USGS, The National Geochemical Survey - database and documentation: U.S. Geological Survey Open-File Report 2004-1001. U.S. Geological Survey: Reston, VA, 2004.
- Walraven, N.; Bakker, M.; van Os, B. J. H.; Klaver, G. T.; Middelburg, J. J.; Davies, G. R., Factors controlling the oral bioaccessibility of anthropogenic Pb in polluted soils. *Science of the Total Environment* 2015, 506-507, 149-163.
- White, P. D.; Marcus, A. H., The Conceptual Structure of the Integrated Exposure Uptake Biokinetic Model for Lead in Children. *Environmental Health Perspectives* 1998, 106, 1513-1530.
- Wu, J.; Norvell, W. A.; Welch, R. M., Kriging on highly skewed data for DTPA-extractable soil Zn with auxiliary information for pH and organic carbon. *Geoderma* 2006, 134, (1 2), 187.
- Yesilonis, I. D.; Pouyat, R. V.; Neerchal, N. K., Spatial distribution of metals in soils in Baltimore, Maryland: Role of native parent material, proximity to major roads, housing age and screening guidelines. *Environmental Pollution* 2008, 156, 723-731.
- Young, A., EPA fails to revise key lead-poisoning hazard standards. *USA Today* 2013.
- Zhu, X.; Yang, F.; Wei, C.; Liang, T., Bioaccessibility of heavy metals in soils cannot be predicted by a single model in two adjacent areas. *Environmental Geochemistry and Health* 2016, 38, (1), 233-241.

2.6. Artwork

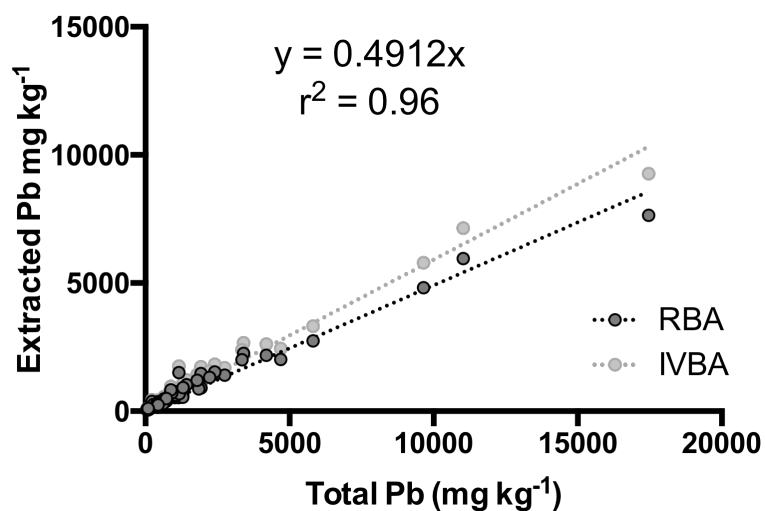


Figure 1. Extractable (bioaccessible) vs. total Pb within contaminated Burlington soils. Transparent symbols represent in vitro bioavailable Pb (IVBA), non-adjusted; opaque symbols represent relative bioavailability, adjusted from IVBA using weighted linear regression. Regression formula and r^2 value represent RBA values only.

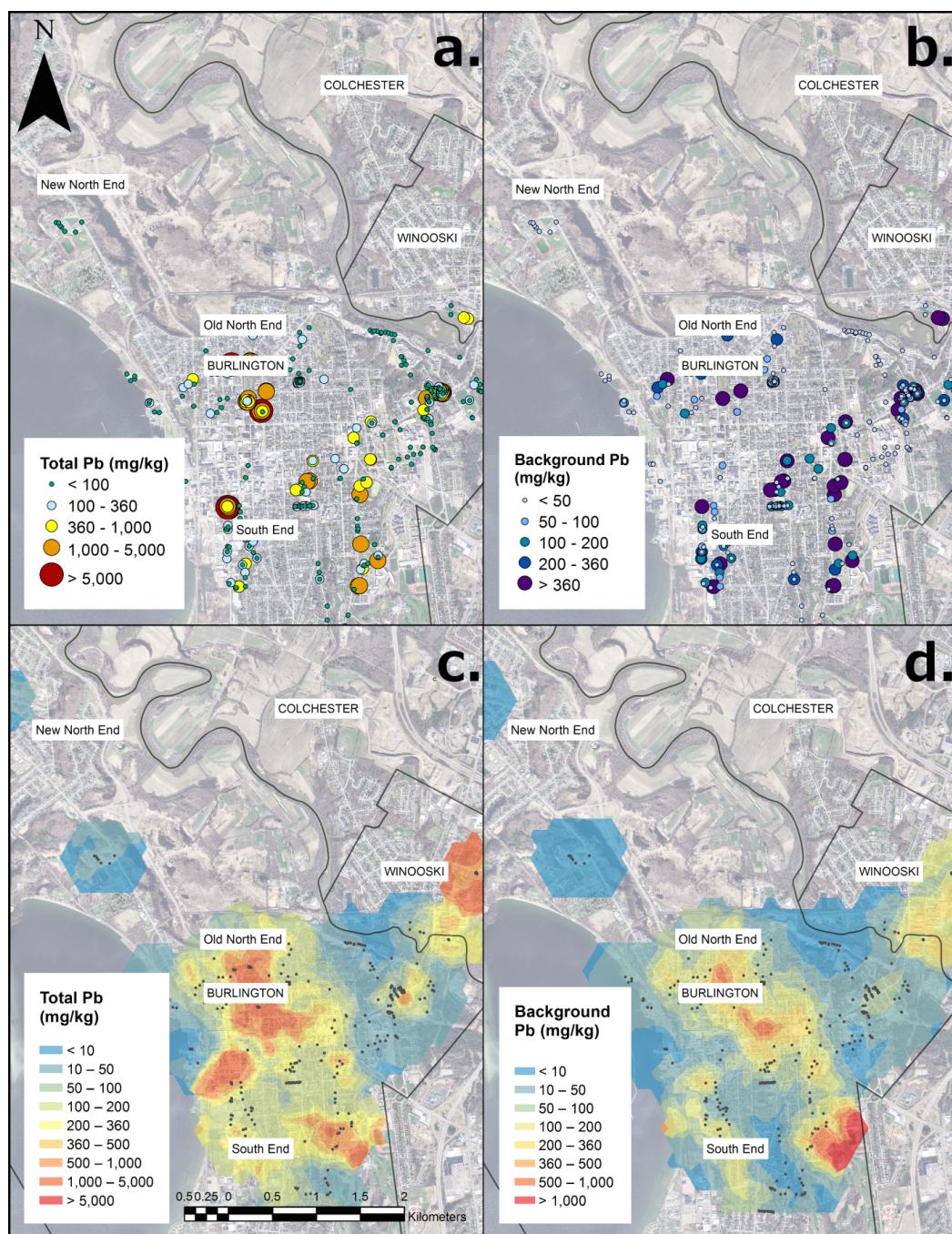


Figure 2. (a) Total Pb distribution in Burlington and surrounding areas. (b) Background Pb distribution in Burlington and surrounding areas. (c) Kriging interpolation showing predicted total Pb distribution in Burlington soil, with sample locations symbolized in black. (d) Cokriging interpolation showing distribution of background Pb in Burlington soil, with sample locations symbolized in black.

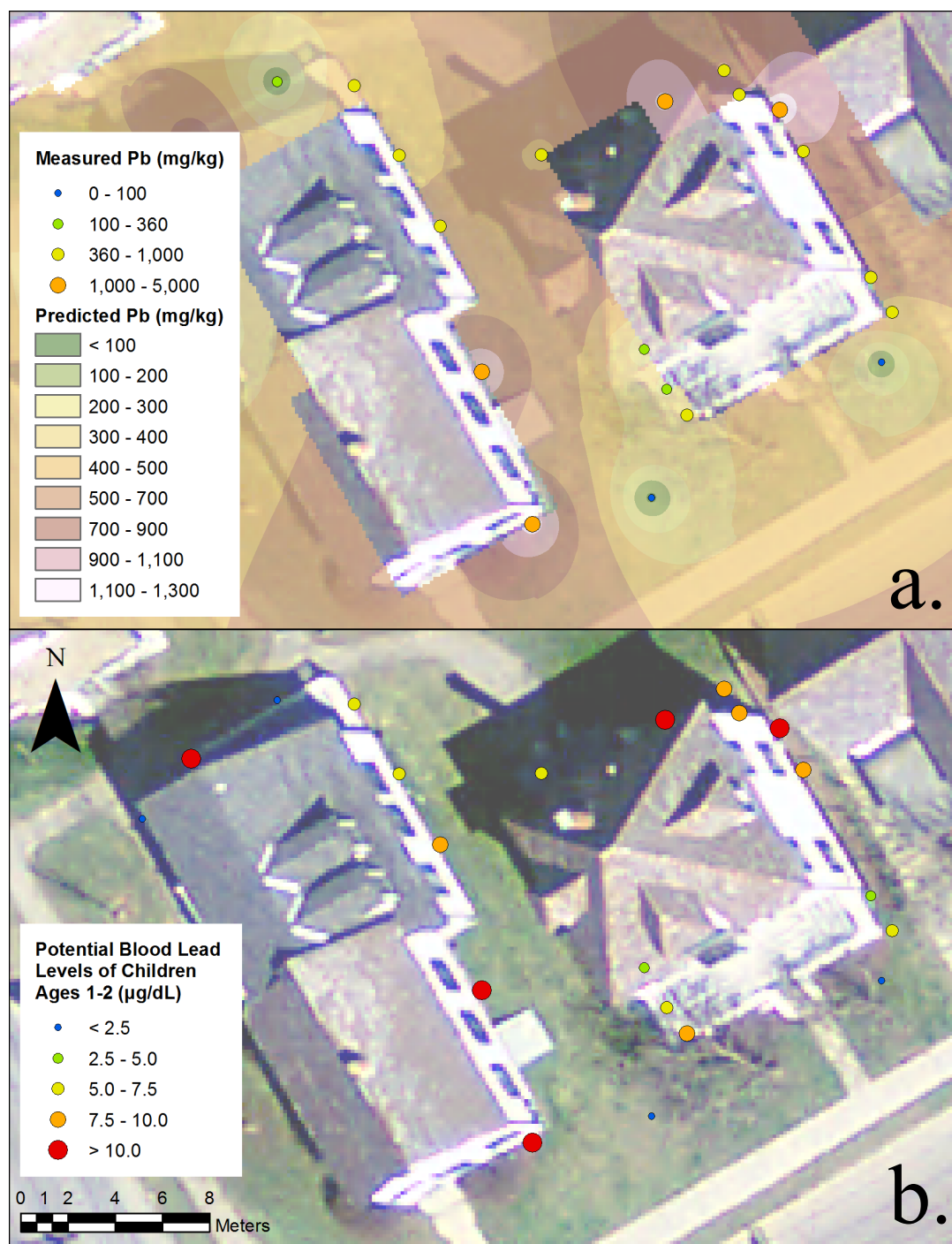


Figure 3. (a) Site-specific inverse data weighting (IDW) interpolation map showing total Pb distribution at two similar structures, with measured concentrations given by circles graduated with increasing Pb concentration and predicted concentrations symbolized by contours. Structure on the left was built in 1880; structure on right was built in 1899. (b) Predicted site-specific health burden of children age 1-2 at two similar structures.

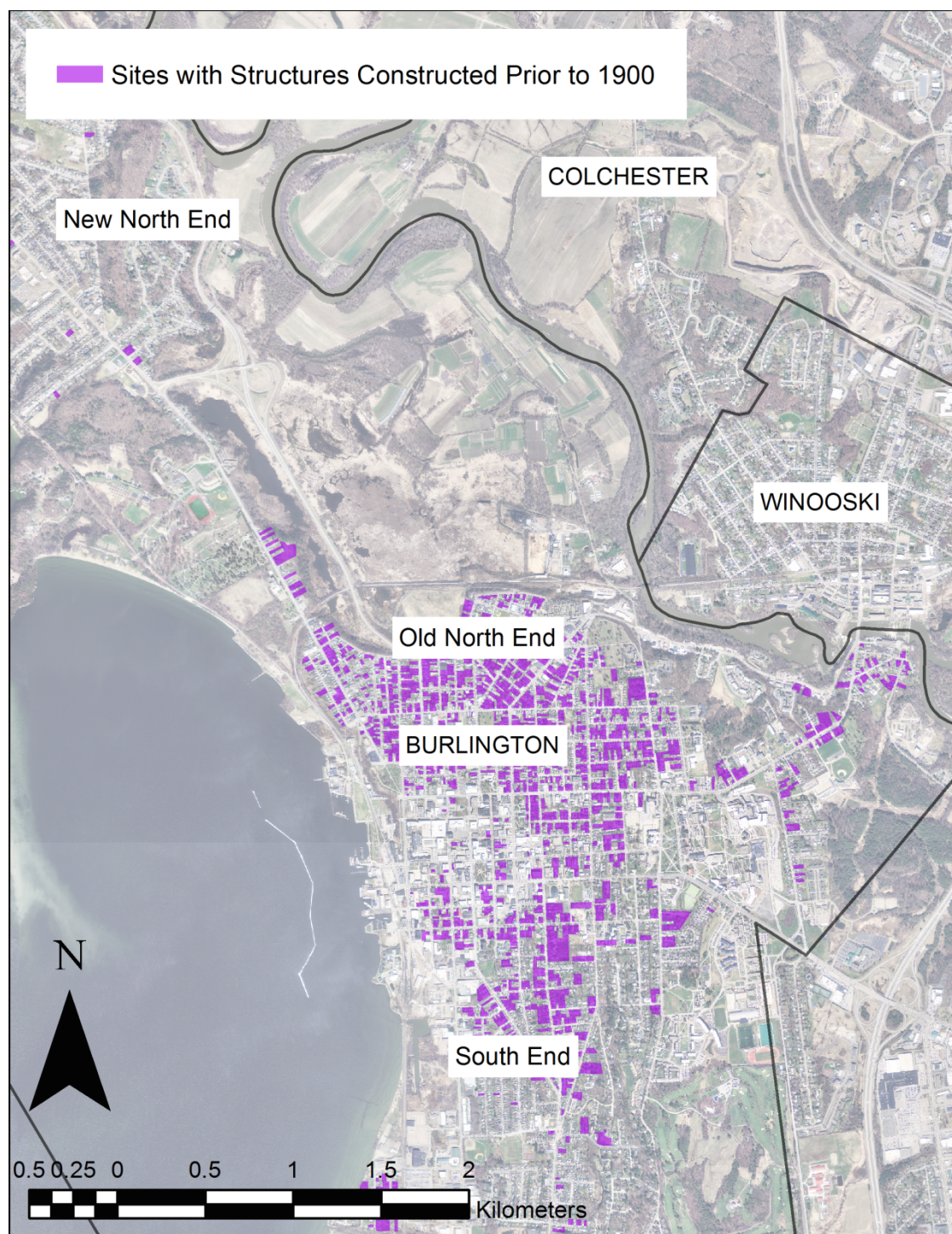


Figure 4. Burlington structures with a predicted maximum health burden exceeding CDC threshold of $5 \mu\text{g dL}^{-1}$.

2.7. Tables

Table 1. Total Pb distribution statistics for samples gathered near Burlington, Vermont.

	Samples within 0.5 m of buildings (mg kg ⁻¹)	Site controls (mg kg ⁻¹)
Mean	1988	328
Median	1047	208
Minimum	51	69
Maximum	17463	1012

CHAPTER 3: Competitive Sorption Dynamics Control Lead Behavior in an Urban Soil at Multiple Scales

For submission to *Journal of Environmental Quality*.

AUTHOR NAMES: Jennifer A. Bower, Chandler Noyes, Andrew Schroth, David Singer, Nicolas Perdrial*

AUTHOR ADDRESS: University of Vermont, Department of Geology, Burlington, VT, 05405-1758.

KEYWORDS: Lead paint, competitive sorption, speciation, bioavailability

ABSTRACT

Efforts to remediate soil Pb using process-based *in situ* techniques have historically met with variable success due to heterogeneity and unpredictability of Pb within soils. The discovery of the PO₄ method of immobilizing Pb through formation of pyromorphite, a Pb phosphate of low bioavailability, was hailed as a promising development for remediation, but field outcomes have not achieved the success of laboratory efforts. Through multiscale analysis, the hypothesis that competitive sorption behavior is impeding the efficiency of Pb-PO₄ sorption is tested and the response of Pb derived from paint is examined within natural and altered soil environments. Eighteen column experiments were conducted using a soil with elevated Pb from paint (~11,250 mg kg⁻¹), amended with varying quantities of goethite and PO₄ for aqueous and solid phase analysis. Pb within paint chips and soil appeared to exhibit a strong attraction to surrounding soil particles, especially the clay mineral fraction. Pb was found to be incorporated into iron oxide-rich aggregates and sorbing to amorphous-like iron oxide grains. Areas of hydrocerussite-comprised paint chips appeared to alter to anglesite post-deposition, a process which may impede pyromorphite formation within urban soils. This finding counters the narrative that Pb becomes less bioavailable over time due to natural pyromorphite formation in urban soils, and suggests the behavior of paint-derived Pb may be more complex across soil environments than previously thought.

3.1. Introduction

The presence of lead in urban and periurban soils poses a long-term risk to ecologic and human health. In the 20th century, the U.S. saw widespread use of Pb before it was banned within paint and gasoline in 1978 and the early 1990s, respectively (with an exception made for aviation fuel, where it is still used today) (Esler, 2015; Mielke et al., 1997). Legacy Pb persists in topsoil long after it has accumulated from anthropogenic inputs, as it shows a strong affinity for organic matter and mineral surfaces in soils (Schroth et al., 2008). In turn, Pb-contaminated soil and dust is concentrated within cities, where older housing is concentrated and contributions from structures and roadways overlap (Mielke et al., 2011). Higher soil Pb levels are correlated with increased blood lead levels (BLLs) within children (Linton et al., 1980; Mielke et al., 1997), particularly low-income children living in urban centers, who typically ingest soil Pb through hand-to-mouth behavior associated with outdoor play and inhalation of Pb-contaminated dust (Laidlaw and Filippelli, 2008). Children face the highest risk, as increased BLLs can accompany impaired cognitive development, though humans of all ages may experience adverse health consequences from Pb exposure (Peterson, 1979). Given that the transmission of soil Pb to children is a preventable phenomenon, disrupting transmission pathways of soil Pb to children and reducing the extent to which soil Pb is absorbed by humans is fundamental to solving this crisis of environmental justice and public health.

Soils are complicated systems, and can function as a sink or source for metals. Large-scale patterns of metal fate and transport are shaped by small-scale changes in reactivity and biogeochemical processes within soil microenvironments (Hesterberg et

al., 2011; Steefel et al., 2015). Within microenvironments, contaminant metals have varying affinities for metal oxides, organic matter, inorganic molecules, and mineral edges, and may bind to sorbents according to spatial distribution, pH, and CEC (Figure 1a). Competitive behavior can occur between these sorbents, impeding immobilization processes such as formation of pyromorphite ($\text{Pb}_5[\text{PO}_4]_3\text{Cl}$), a Pb mineral with low solubility and high stability under most environmental conditions (Nriagu, 1973) (Figure 1b). In turn, metal sorption affinities and resulting speciation determine contaminant bioavailability, a measure of the extent to which the metal may be absorbed by organisms (Shahid, 2012). Owing to its high electronegativity, Pb is strongly sorbed by functional groups on mineral surfaces and organic matter, and forms strong inner-sphere complexes with humic-like substances and Fe- and Mn-oxides and oxyhydroxides (An et al., 2015; Kaste et al., 2006; Schroth et al., 2008), even forming ternary complexes with sorbents. The relationship between organic matter and Pb is complex, as solid organic matter can efficiently immobilize Pb, but aqueous organic matter can actually increase mobility (Reeder et al., 2006). PO_4 is an effective sorbent of Pb and may complex with aqueous Pb before precipitating as amorphous, poorly crystalline or well-crystallized pyromorphite, all phases which have reduced bioavailability and solubility (Juhasz et al., 2014). The overall affinity for soil constituents means Pb is well-retained where it is deposited and has limited mobility. Pb concentration and distribution affect these rules to a degree, with higher concentrations of Pb overloading soil reactive sites and leading to higher mobility, and varying spatial distribution of Pb sources, i.e. chalking paint vs. corroding bullets, as well as differences in speciation impacting the extent to which Pb is labile. Within this

study area, Pb has been deposited in soil primarily due to exterior weathering of painted structures, a byproduct of its sustained use within historical paint until 1978. Pb was added to paint in a variety of carbonate and sulfate forms, the former predominating when Pb was used as a complete pigment, and was prized for its durability, opacity, and tendency to “chalk” off instead of flaking as it weathered from surfaces (Hunt, 2016). As its toxicity became apparent, Pb was phased out of paint, with TiO_2 and ZnO replacing lead carbonate forms such as basic lead carbonate, or hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}[\text{OH}]_2$). Pb paint remains on many structures today, especially in Burlington, Vermont, a city with a high concentration of wood-frame houses constructed prior to the turn of the 20th century. Although the speciation of Pb within paint formulations is known, the speciation of Pb paint in soil post-deposition has not been examined using microfocused techniques.

Phosphate remediation, a process-based approach designed to reduce Pb mobility and bioavailability, may be the most attractive *in situ* method for reducing the risk of Pb in soils (Cotter-Howells and Caporn, 1996; Ruby et al., 1994; Scheckel et al., 2013; Schwab et al., 2006). This method relies on the ability of PO_4 to sorb strongly with Pb and coprecipitate to form pyromorphite, possessing low solubility as described above. Low solubility reduces the extent to which the lead is bioavailable, a measure of how readily it is absorbed by organisms (Cao et al., 2002). The effectiveness of *in situ* treatments is complicated by the heterogeneity of soils, and the phosphate method is no exception. Differing soil conditions and processes impede the reliability and efficiency of PO_4 – Pb sorption in natural soils, presenting a barrier for implementation (Cotter-Howells and Caporn, 1996; Scheckel et al., 2013). PO_4 is a strong sorbent of Pb in soils

under most pH conditions, but if reactive sites are already occupied or Pb is not present in free ionic form, then the process of immobilization may be impeded. PO_4 may compete for Pb with other sorbents such as iron oxides and oxyhydroxides and soil organic matter. By adjusting sorbent ratios to favor free Pb and PO_4 , this method may be refined for maximum efficiency. Amendment with a high-solubility phosphate species or acidification of soil can also increase pyromorphite formation efficiency, but these methods can prove problematic in areas of high phosphorus loading and negatively impact soil health (Miretzky and Fernandez-Cirelli, 2008; Weber et al., 2015).

In view of these considerations, work is needed to characterize and predict the behavior of Pb derived from weathering paint in complex soil systems. A guiding objective of this study is to investigate soil Pb behavior at multiple scales within near-field flow-through experiments conducted on a single Pb-impacted soil in response to increased competitive sorbents. This is conducted with the hypotheses that Pb mobility is controlled by low pH, addition of PO_4 will reduce the extent to which Pb is mobilized, and increased goethite may occupy reactive sites on organic matter and result in more Pb available to bind to PO_4 . These resulting mechanisms are then examined at a microscopic scale using SEM-EDS and microfocused synchrotron-based x-ray techniques, with the additional goal of investigating the premise that hydrocerussite is a major species within Pb paint and that species transformation may occur after it is deposited in soil.

3.2. Materials and Methods

3.2.1. Soil Characterization

A single soil sample was augered from the top 10 cm of a residential site in Burlington, VT, contaminated with Pb derived from chipping exterior paint. The sample was air-dried and large chunks of organic material removed. Half was saved, and the other half dry-sieved through a 2 mm fine mesh sieve.

Sieved sample was analyzed for particle size using a Beckman Coulter LS 230 particle size analyzer equipped with a sonicating circulation attachment, and a fraction was powderized to *ca.* 100 μm for five minutes in a tungsten carbide ball mill and reserved for XRD, XRF, and elemental carbon analysis.

A CE elemental analyzer was used to measure total carbon content through dry combustion of *ca.* 50 mg sieved soil, and calibrated using standard soil B2152 (Elemental Microanalysis Limited, 2016). Bulk mineralogy was determined using a Rigaku benchtop X-ray diffractometer with Cu K α radiation operated at a wavelength of 1.54178 Å in a 2 theta range of 3-75° and a counting time of 0.02° (2 theta) per minute. Fine fraction of soil (<40 μm) was separated using the procedure from Perdrial et al. (2014) by suspending sediment in ethanol and sonicating for 5 minutes, then removing suspended particles with a pipette into a weighing dish for air-drying. Fine fraction was then analyzed with XRD using the same settings described above. Resulting diffractograms were qualitatively characterized using the ICDD database and quantified using Rigaku PDXL. Total Pb was measured with a Thermo Scientific Niton XL3t 900 series portable XRF, calibrated with soil standard NIST 2780 (NIST, 2012),

with a counting time of 60 seconds and readings averaged in triplicate. Sample contained *ca.* 11,250 mg kg⁻¹ (± 91.8) Pb.

Lead bioaccessibility in sieved sample was determined by extraction with a solution of acidified glycine in an incubator according to EPA method 1340 (EPA, 2013). Sieved fractions of soil totaling one gram (± 0.05 g) were suspended in 100 \pm 0.5 mL of 0.4 M glycine solution, acidified to pH 1.5 using ultrapure HCl, after which they were heated to 37 \pm 2 °C and shaken at 300 rpm for an hour within a BioMaker BS-ES-60 orbital incubator shaker. Following digestion, 40 mL of solution was sampled with a syringe and filtered through a 0.45 μ m GHP filter. After dilution with 1% ultrapure HNO₃, the solution was analyzed for extracted Pb using a Jobin Yvon Horiba ICP-OES mono line at 220.353 nm and a standard curve ranging from 0.5 to 10.0 mg L⁻¹. Digestions were performed in duplicate. The *in vitro* relative bioavailability (IVBA) was then calculated and relative *in vivo* bioavailability (RBA) adjusted using a weighted linear regression according to equations included in EPA method 1340 (EPA, 2013).

For microscale analysis, a thin section of contaminated soil was prepared. A fraction (~2g) of sieved sample was packed into a PPCO column 2.1 cm long and 0.9 cm in diameter, capped, and injected with EPO-TEK 301 spectrally transparent epoxy. After removal from the column, the hardened tube of soil was thin sectioned to a 30 μ m final thickness and mounted with acrylic using Crystalbond 509 on 27x46mm borosilicate glass, after which it was microprobe polished with 0.5 μ m diamond (Spectrum Petrographics). Once thin section was prepared, it was carbon coated under vacuum and examined using a Tescan Vega 3 LMU scanning electron microscope with

Oxford energy dispersive spectroscopy attachment. Before further microscale elemental analysis was conducted, thin sections were separated from glass mount by soaking in acetone to avoid interference by trace As within glass. The samples were analyzed by microfocused XRF mapping at beamline 13-IDE (Newville et al., 1999) at the Advanced Photon Source with a beam size of 1.5x1.5 μm at full width half maximum subjected to a Pt-coated Kirkpatrick-Baez focusing optics system (XRadia), and using a Vortex four-element Si drift diode array detector operating at 18 keV. Fifteen XRF maps were generated as 500x500 μm maps at 2 μm pixel size and dwell time of 30 ms per pixel for elements K, Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, and Pb, and analyzed by normalizing to the measured intensity of the incident energy of the x-ray beam (I_0) using Larch (Newville, 2013). Selected grains were subjected to microfocused XRD analysis at the same beamline in transmission mode with an area CCD camera with incident beam energy of 18 keV ($\lambda = 0.6888 \text{ \AA}$). Images were converted from 2D to 1D diffraction patterns using Area Diffraction Machine (Lande, 2013), with sample distance and geometry corrected using CeO_2 as a standard. QualX (Altomare et al., 2008) was used to subtract background and perform phase identification, referencing likely mineral patterns available from the Crystallographic Open Database (Gražulis et al., 2009).

3.2.2. Column Experiments

A sieved, unground fraction of the sample, containing $\sim 11,250 \text{ mg kg}^{-1}$ Pb (± 91.8), was selected for column preparation. Eighteen columns were assembled by packing with *ca.* 1.8 g of sieved sediment into 0.9 cm (internal diameter) by 2.1 cm (pack length) polypropylene copolymer columns, with a 20 μm polytetrafluoroethylene

frit inserted at either end, and a 0.45 μm membrane polypropylene filter under the cap on the effluent-out end, giving an average pore volume of 0.82 cm^3 and average porosity of 55.03%. To determine the pH at which Pb was most effectively mobilized, three columns were leached with synthesized rainwater prepared using a method modified from Wang et al. (2011) (Table 1), adjusted with HCl and KOH to a pH of 3, 4, and 5, respectively. Configuration of column experiment setup is depicted in SI Figure 4.

Once it was established that Pb was solubilized most readily at a pH of 3, synthetic rainwater was adjusted to pH of 3 using ultratrace HCl for 2 additional column experiments. Then it was amended with 3 mM PO_4 and adjusted to a pH of 3 using KOH for 4 other columns to test the impact of PO_4 on Pb mobilization. Rainwater was leached through the prepared columns at a flow rate of approximately 0.05 mL min^{-1} , with effluent collected in sample tubes in 120-minute increments for 96 hours using a Foxy 200 fraction collector. The composition of all rainwater configurations used in column experiments is given in Table 1. To test the impact of higher iron oxide content on Pb mobility and bioavailability, 9 columns were packed with soil that was homogeneously mixed with 0.57, 1.14, and 2.28 g kg^{-1} goethite ($\text{FeO}(\text{OH})$) soil, respectively. $\text{FeO}(\text{OH})$ was synthesized by adding 0.2 L of 2.5 M KOH to 50 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 0.825 L of 18 $\text{m}\Omega \text{ cm}^{-1}$ water and heating the solution at 60° C for 24 hours (Linker et al., 2015). Solids were washed with 0.1 mM HCl and centrifuged using a Thermo IEC Centra C13 centrifuge until a supernatant pH of ~5 was achieved, and clods were dispersed using an agate mortar before $\text{FeO}(\text{OH})$ was mixed with soil. Mineralogical identity was corroborated by color reference guide (Schwertmann and

Cornell, 1992) and by submitting c. 1 g of material to x-ray diffraction analysis, which confirmed precipitate was homogeneously composed of poorly crystalline goethite. A complete inventory of column preparations and replicates is given in Table 2.

3.2.3. Column Analysis

Column effluent was analyzed for a range of elements in solution. After dilution with nanopure water, inorganic and non-particulate organic carbon was measured with a Shimadzu TOC-L Analyzer. A Fisher Accumet AB15 gel-filled probe was used to determine pH. Anion (Cl^- , NO_3^- , PO_4^{2-} , SO_4^{2-}) concentrations within undiluted and 4x diluted samples were determined by ion chromatography (Dionex LC20) and metals and metalloids (Pb, Fe, Al, Na, Mg, K, Mn, Ca, P) concentrations within 20x diluted samples by ICP-OES (Horiba).

Post-leaching solid phase analysis was conducted by examining thin sections of two columns leached with phosphate and amended with goethite, respectively, prepared as detailed above, and analyzed using SEM-EDS and synchrotron-based μXRF and μXRD techniques.

Bioaccessibility of Pb in columns leached with rainwater containing PO_4 only, and leached with rainwater containing PO_4 and amended with 0.06% and 0.13% $\text{FeO}(\text{OH})$, respectively, was determined with EPA method 1340 as mentioned previously, with extraction performed in duplicate for each preparation.

3.3. Results and Discussion

3.3.1. Soil Characterization

Preliminary characterization of target soil was performed through analysis of sediment size, mineralogy, Pb content, bioaccessibility, and carbon analysis (Table 3).

Particle size distribution is consistent with a loamy sand soil, a designation that is congruent with the local soil type, the Windsor loamy sand. Visual inspection of soil indicated that paint chips were present in grains large enough to be seen with the naked eye. Carbon content was measured to be 0.0749 g g^{-1} . Powder diffraction analysis within bulk and fine fractions reflects the presence of goethite and clay minerals in a quartz-rich soil. Though bulk soil was chosen for its elevated Pb levels ($\sim 11,250 \text{ mg kg}^{-1}$), crystalline Pb species were undetected by diffraction in bulk and fine fractions. Bioaccessibility results of unleached and leached soil are given in Table 4. Columns leached with acidified rainwater but unamended with FeO(OH) exhibited the highest average fraction of bioaccessible Pb ($0.767 - 0.768$), while native unleached soil and columns amended with goethite exhibited a lower percentage of bioaccessible Pb ($0.596-0.675$). The bioaccessibility of Pb within sieved, unleached soil (0.675 ± 0.006) is higher than the area average for Burlington soils (~ 0.491 ; see Bower, et al., 2017), indicating that a higher proportion of Pb is found within soluble species at this location compared to the whole. The relatively high bioaccessibility of Pb within columns unamended with FeO(OH) but leached with acidified rainwater compared to Pb within columns amended with FeO(OH) suggests that FeO(OH) might have a small role in mitigating the solubilization of Pb, leading to a slight reduction in the bioaccessibility of Pb in paint-impacted environments. This effect could be attributed to the strong affinity between Pb and iron oxides and oxyhydroxides. More work is needed to study the potential effects of FeO(OH) on Pb bioavailability in near-field soils, as it is suspected that the concentrations of FeO(OH) added within these experiments may have not been enough to significantly alter Pb dynamics for this soil. The risk of

dissolving soil pyromorphite phases during the glycine extraction used in the EPA protocol due to low pH (~1.5) has been identified (Zia et al., 2011), however, other work has suggested that *in vitro* assays conducted at a higher pH may risk forming pyromorphite through extraction with glycine, further complicating efforts to estimate soil bioavailability (Scheckel et al., 2013). Still, *in vitro* glycine digestion is preferred over multi-phase or sequential extractions for estimating bioaccessibility, and has been verified through *in vivo* testing (Deshommes et al., 2012; Rasmussen et al., 2011).

3.3.2. Column Effluent

Column effluent was collected at intervals of approximately 7 “pore volumes” (PV), a volumetric unit incorporating rate of flow to represent the filling of an average soil pore, which serves as a proxy for time. Concentration of selected elements (defined above) and pH were measured within column effluent over the course of experiments. Results of preliminary leaching experiments indicated that eluent at a pH of 3 is favorable for Pb mobilization, suggesting that Pb was present in species prone to dissolution at low pH, such as lead carbonates (hydrocerussite, cerussite) common to Pb paint. Successive column experiments were conducted at a pH of 3. Mean Pb concentration and pH of columns over PV according to column preparation are given in Figure 2. Pb release initiated within columns when effluent reached a pH of approximately 4.9. The kinetics of Pb release in response to further acidification differed according to column preparation; within columns leached with phosphate-amended rainwater, pH of column effluent appeared to achieve pseudo-equilibrium at a pH of ~3.25, with Pb release plateauing as pH stabilizes. Columns leached with HCl-amended rainwater exhibited more gradual acidification, and Pb release, though slower

to initiate, never reached this plateau. Results of elemental analysis and pH measurement are given in Figure 3. Ca concentration in effluent exhibited a sharp rise during acidification of soil columns and decreased until experiments terminated. K, Na, and P increased in concentration at the beginning of experiments and plateaued as experiments progressed. Total Pb concentration was calculated for single soil columns based on weight of column soil and used in concert with Pb concentration in effluent to compute percentage of Pb remaining in soil columns (Figure 3). A max of 11.1% of the estimated total of Pb within columns was desorbed.

The dependence of Pb mobilization on pH reveals that within this soil environment, Pb release is controlled by acidification. Though Pb was solubilized within every column conducted at pH of 3, differences between column behavior in response to the presence or absence of PO_4 and added $\text{FeO}(\text{OH})$ are minor. The uptake of P in the beginning of column experiments, suggested by the steep rise in P as rainwater saturates available P binding sites in soil, leaving P free to flow through, indicates that P is sorbing to soil components, potentially binding with some of the Pb species released during acidification. Concentration of K exhibits similar behavior, likely retained by clay interlayers in column soil as it flows through.

Column soil was sieved and homogenized prior to column preparation, but it is expected that Pb content was still unequal across columns. One column exhibited a far higher release of Pb than other columns. Considering the heterogeneous distribution of Pb particles within this soil and presence of differently-sized paint chips, it is hypothesized that this column contained a quantity of soluble Pb, possibly in the form

of a large paint chip, higher than the column mean. This finding highlights the complexity inherent to studying soils in near-field systems.

3.3.3. Microcrystalline and Elemental Analyses of Solid Phase

SEM-EDS analyses of native soil indicated fine particles of Pb are distributed throughout soil. Pb was also present in the form of large Pb-rich particles, layered with titanium (Ti) (Figure 4a) and zinc (Zn), common constituents within non-Pb based paint formulations. Large particles enriched in Pb appeared physically weathered, with zones of varying relative levels of Pb and holes or mineral inclusions disrupting the homogeneity and structure of the overall particle. In one striking example, a rind of aluminosilicates outlines a cracked layer of Pb that in turn encases a carbon-rich center (Figure 4b). Figure 4c depicts an area rich in Pb that appears to be heavily weathered, owing to its patchwork-like appearance, and consists of three distinct zones: an area rich in Pb, with some silicate minerals appearing to be sorbed to the edges; a zone comprised of Pb and Ti that appears to contain inclusions rich in Mg and Si, and finally a zone enriched in Ti and Cr.

Distribution of fine particles of Pb in areas of the soil matrix is consistent with the method of weathering exhibited by Pb paint, known as “chalking”, where Pb erodes from exterior surfaces in the form of a fine powder (Davis and Burns, 1999), a form of erosion that would have occurred before the banning of Pb paint in 1978. The presence of Pb within large particles in association with Ti and Zn is a finding compatible with erosion patterns of more recent paint formulations, which breaks off from painted surfaces in flakes, carrying the underlying layers with it and preserving multiple generations of paint in partitioned paint flakes such as the particle visible in Figure 4c.

The presence of large, stratified Pb-bearing particles is morphologically unique to Pb derived from paint for this location, as gasoline-derived Pb is dispersed in aerosol form. A key example is given in Figure 4b, which is interpreted as a wooden splinter from a painted structure with Pb paint adhered to the exterior. The titanium flecks adjacent to this splinter may reflect a later generation of paint. This image is valuable for its representation of Pb weathering *in situ*; the Pb adhered to the splinter has developed deep grooves, and smaller particles of Pb are visible within the rind of soil particles outlining the main Pb layer. Furthermore, it shows the attraction between Pb paint and clay minerals, which implies that Pb is interacting with surrounding soil components. In this way, it appears that Pb from paint has become a fundamental component of the soil fabric in this area through weathering processes. This interaction is also observed in Figure 4c (larger view given in SI Figure 5), where aluminosilicate minerals are visible within a heavily weathered paint chip. The complex elemental stratification and composition of this paint chip requires that the elemental composition of common paint formulations be cross-referenced to aid in the identification and interpretation of its foundational components. The microscopic view of this paint chip is hypothesized to depict a cross-sectional view perpendicular to the plane of paint application and building exterior surface. Chromium oxide (CrO) and titanium dioxide (TiO₂) are likely the species present within the upper layer of the chip in Figure 4c, with CrO giving the recent paint coating its greenish tint and TiO₂ serving as the white base. The zone containing Mg and Si represents a less obvious paint derivative, as it consists of a zone of Mg- and Si-enriched particles of varying sizes. According to industrial sources (<http://www.mondominerals.com/>), the principal ingredient in primer formulations is

hydrated magnesium silicate ($\text{H}_2\text{Mg}_3[\text{SiO}_3]_4$), or as it is known by its mineral form, talc. Therefore, this zone is probably a layer of primer that was applied on top of the old lead paint layer before the most recent layer of paint was applied. An interesting feature of this primer layer is that both Pb and Ti are present in smaller concentration than the paint layers. This suggests that Pb and Ti in the underlying and overlying layers have migrated. There are two possible mechanisms for this incorporation: one, the primer picked up fine Pb particles as it was applied from the base layer, with Ti permeating into the primer once it was applied on top; two, passive elemental transfer (diffusion) occurred post-application through exposure to environmental wetting/drying patterns that allowed mobility through a fluid interface. When this EDS map is contextualized within the larger view captured under the SEM, it stands as a piece of a greater zone of high reflectance (area of probable Pb and Ti enrichment), representing the larger contiguous paint chip. Pores are visible within chip, which may derive from the thin section microprobe polishing process or through weathering processes. Within left corner of image a zone of disintegrating paint is observed, with more porosity and grain disorder than main area of chip. Physical weathering of paint is hypothesized to increase the bioavailability of Pb, by redistributing it such that it attains a higher surface area and thus possesses greater reactivity within soil. The ramifications of soil acidification and changing geochemical conditions are therefore magnified when applied to scattered fine particles of Pb, in contrast to affecting only the outer boundary of cohesive Pb paint chip.

Synchrotron work enables the linking of μXRF elemental data with identification of crystalline material through targeted μXRD analysis. Soil components

akin to those identified through SEM elemental analysis are visible within μ XRF maps, identified by μ XRF maps (Figures 5-6), elemental correlations, and spot μ XRD identification of crystalline material. Main soil components included feldspar minerals, quartz particles, clays, and amorphous zones consisting of iron oxides and assorted metals, likely aggregated by organic matter. The incorporation of Pb within soil aggregates indicates that once deposited, Pb has a profound interaction with the soil in this area not limited to electrostatic attraction; it is becoming a fundamental part of the soil fabric. The presence of Pb within Fe-rich aggregates and in association with Fe in small particles (Figure 5) suggests that Fe oxides are a vehicle for redistributing Pb within this soil. Identification of Ti within aggregates and sorbed to mineral surfaces near eroding paint chips also suggests that recent paint coatings constitute a source of Ti for this soil. Elemental correlations revealed spatial relationships between Pb and Zn, Pb and Cr, Ti and Ca, Mn and Fe, and others (SI Figure 6). These correlations denote elemental associations within paint as well as within local soil minerals (i.e. a zone with robust Al-K-Fe correlation indicates a grain of biotite). Pb, Zn, Cr, Ti are common elements within paint compounds; Mn and Fe are associated with oxides and oxyhydroxides, and serve as reactive constituents of soil aggregates. Soil aggregates are comprised of elements congruent with clay minerals (K, Al, Ca) and Fe phases (Figure 5), and contain discrete zones and particles of Pb and Ti, along with other elements found within paint components (Zn, Cr). For the purposes of this study, lead bearing minerals were prioritized within XRD investigation. The identity of Pb species was established within each soil treatment subjected to XRD. The primary Pb-bearing minerals identified through phase analysis include hydrocerussite, cerussite,

pyromorphite, and anglesite. One μ XRF map appears to contain a particularly large grain made of Pb (Figures 6, expanded figure given in SI Figure 7) with an outer layer of Zn, of which the area of highest Pb concentration was determined to be comprised of hydrocerussite, a lead carbonate ($\text{Pb}_3[\text{CO}_3]_2[\text{OH}]_2$), through μ XRD analysis (Figure 6). An XRD pattern was collected at a point within a less-dense area of this grain enriched in iron and was determined to contain anglesite, a lead sulfate (PbSO_4), with no iron-bearing minerals identified in the pattern. The finding that hydrocerussite is a principle species in this soil, especially in the Pb-dense paint chip, is congruent with its role as a main component of lead paint. Zn-rich layer on paint chip within this figure suggests that a more recent coating of paint was applied before Pb chip weathered from structure. The discovery of anglesite at numerous points within this soil suggests that Pb speciation has evolved over time, especially since anglesite was identified at a spot in the paint chip in Figure 6 within a zone that appears to have weathered slightly. Because no Fe phases were identified within this diffraction pattern, we interpret the Fe enrichment of this spot to indicate that non-crystalline or amorphous iron oxides are binding to anglesite in this location, a finding that correlates with previous work supporting the strong affinity of amorphous iron oxides to Pb (Kaste et al., 2006). The change in speciation from cerussite to anglesite during the weathering process has been observed in soil at sites impacted by mining activity (Davis et al., 1992) but has not previously been documented within soils affected by Pb paint. Cerussite is the primary Pb species at alkaline pH given standard conditions and in the presence of PO_4 and other ions, but below a pH of 4.6, anglesite and pyromorphite predominate, as shown in stability diagram in Figure 15. The low pH of the Windsor series supports the alteration

of cerussite to anglesite, and it is expected that this alteration would occur in other acidic soil in the Northeast contaminated with Pb paint.

A few studies have predicted that Pb in urban soils is becoming less bioavailable over time, as garden soils are amended with compost and organic matter containing PO_4 and Pb binds with amorphous iron oxides and soil organic matter (Walraven et al., 2015; Zia et al., 2011). While Pb phases are observed to partition to less soluble forms in soil, the timing of this process is dependent on factors such as particle size, local pH, encapsulation, and availability of binding partners. Although the alteration of cerussite to anglesite places Pb in a less soluble form, anglesite is still a relatively bioavailable form of Pb compared to recalcitrant pyromorphite phases (Hunt, 2016). For this reason, the transformation to anglesite may reduce the efficiency of PO_4 remediation, as this Pb form leaves Pb unavailable for binding to PO_4 and as it is a species that is stable at low pH. The combined effect of iron oxide sorption and alteration to anglesite appears to present a barrier to pyromorphite formation within this urban soil; it is expected that the availability of SO_4 and iron oxides, as well as the amount of organic matter, will affect these dynamics in other soils.

Acknowledgements

We thank David West for his assistance with using the SEM at Middlebury College. Much gratitude is due to David Singer for his generosity in providing beam time at the Advanced Photon Source (APS) and for his assistance with processing data. Funding support from the Vermont Geological Society made travel to the APS possible. Part of this work was performed at GeoSoilEnviroCARS (Sector 13), APS, Argonne National Laboratory. GeoSoilEnviroCARS (Sector 13) is supported by the National

Science Foundation – Earth Sciences (EAR-1128799) and Department of Energy-GeoSciences (DE-FG02-94ER14466). Use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

3.4. References

- Altomare, A.; Cuocci, C.; Giacobazzo, C.; Moliterni, A.; Rizzi, R., QUALX: a computer program for qualitative analysis using powder diffraction data. *Journal of Applied Crystallography* 2008, 41, (4), 815.
- An, J.; Jho, E. H.; Nam, K., Effect of dissolved humic acid on the Pb bioavailability in soil solution and its consequence on ecological risk. *Journal of Hazardous Materials* 2015, 286, 236-241.
- Cao, X.; Ma, L. Q.; Chen, M.; Singh, S. P.; Harris, W. G., Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. *Environmental science & technology* 2002, 36, (24), 5296.
- Cotter-Howells, J.; Caporn, S., Remediation of contaminated land by formation of heavy metal phosphates. *Applied Geochemistry* 1996, 11, (1), 335-342.
- Davis, A. P.; Burns, M., Evaluation of lead concentration in runoff from painted structures. *Water Research* 1999, 33, (13), 2949-2958.
- Davis, A.; Ruby, M.; Bergstrom, P., Bioavailability of arsenic and lead in soils from the Butte, Montana, mining district. *Environmental Science & Technology* 1992, 26, (3), 461.
- Deshommes, E.; Tardif, R.; Edwards, M.; Sauvé, S.; Prévost, M., Experimental determination of the oral bioavailability and bioaccessibility of lead particles. *Chemistry Central Journal* 2012, 6, (1), 138.
- Elemental Microanalysis Limited, Certificate of Analysis: Low Organic Content Soil OAS. In CatNo B2152 - Certificate No. 207835, Devon, England, 2016.
- EPA, In Vitro Bioaccessibility Assay for Lead in Soil. SW-846 2013, (1340), 24.
- Esler, D., Getting the lead out: the future of avgas.(unleaded aviation gasoline)(Operations). *Business & Commercial Aviation* 2015, 111, (2), 30.
- Gražulis, S.; Chateigner, D.; Downs, R. T.; Yokochi, A. F. T.; Quirós, M.; Lutterotti, L.; Manakova, E.; Butkus, J.; Moeck, P.; Le Bail, A., Crystallography Open Database – an open- access collection of crystal structures. *Journal of Applied Crystallography* 2009, 42, (4), 726-729.
- Hesterberg, D.; Duff, M.; Dixon, J.; Vepraskas, M., X- ray Microspectroscopy and Chemical Reactions in Soil Microsites. *Journal of Environmental Quality* 2011, 40, (3), 667-78.
- Hunt, A., Relative bioaccessibility of Pb-based paint in soil. *Environmental geochemistry and health* 2016, 38, (4), 1037.

- Juhasz, A.; Gancarz, D.; Herde, C.; McClure, S.; Scheckel, K.; Smith, E., In Situ Formation of Pyromorphite Is Not Required for the Reduction of in Vivo Pb Relative Bioavailability in Contaminated Soils. *Environmental Science & Technology* 2014, 48, (12), 7002.
- Kaste, J.; Bostick, B.; Friedland, A.; Schroth, A.; Siccama, T., Fate and Speciation of Gasoline- Derived Lead in Organic Horizons of the Northeastern USA. *Soil Science Society of America Journal* 2006, 70, (5), 1688-1698.
- Laidlaw, M. A. S.; Filippelli, G. M., Resuspension of urban soils as a persistent source of lead poisoning in children: A review and new directions. *Applied Geochemistry* 2008, 23, (8), 2021-2039.
- Lande, J., Area Diffraction Machine v1.0.4. 2013.
- Linker, B.; Khatiwada, R.; Perdrial, N.; Abrell, L.; Sierra-Alvarez, R.; Field, J.; Chorover, J., Adsorption of novel insensitive munitions compounds at clay mineral and metal oxide surfaces. *Environmental Chemistry* 2015, 12, (1), 74-84.
- Linton, R. W.; Natusch, D. F. S.; Solomon, R. L.; Evans, C. A., Physicochemical characterization of lead in urban dusts. A microanalytical approach to lead tracing. *Environmental Science & Technology* 1980, 14, (2), 159-164.
- Mielke, H. W.; Dugas, D.; Mielke, P. W.; Smith, K. S.; Gonzales, C. R., Associations between soil lead and childhood blood lead in urban New Orleans and rural Lafourche Parish of Louisiana. *Environmental Health Perspectives* 1997, 105, (9), 950.
- Mielke, H.; Gonzales, C. R.; Mielke, P., The continuing impact of lead dust on children's blood lead: Comparison of public and private properties in New Orleans. *Environmental Research* 2011, 111, (8), 1164-1172.
- Miretzky, P.; Fernandez-Cirelli, A., Phosphates for Pb immobilization in soils: a review. *Environ Chem Lett* 2008, 6, (3), 121-133.
- Newville, M., Larch: An Analysis Package for XAFS and Related Spectroscopies. *J. Phys.: Conf. Ser.* 2013, 430, 012007.
- Newville, M.; Sutton, S. R.; Rivers, M. L.; Eng, P., Micro- beam X- ray absorption and fluorescence spectroscopies at GSECARS: APS beamline 13ID. *J Synchrotron Rad* 1999, 6, (3), 353-355.
- NIST, Certificate of Analysis: Standard Reference Material 2780. In *Hard Rock Mine Waste*, National Institute of Standards & Technology: Gaithersburg, MD, 2012; p 4.

- Nriagu, J. O., Lead orthophosphates—II. Stability of chlopyromophite at 25°C. *Geochimica et Cosmochimica Acta* 1973, 37, (3), 367-377.
- Perdrial, N.; Thompson, A.; O'day, P. A.; Steefel, C. I.; Chorover, J., Mineral transformation controls speciation and pore- fluid transmission of contaminants in waste- weathered Hanford sediments. *Geochimica et Cosmochimica Acta* 2014, 141, 487-507.
- Peterson, J., Pb: Advances in Research on Effects of Lead on Children's Behavior and Intelligence. *Ambio* 1979, 8, (5), 223-226.
- Rasmussen, P.; Beauchemin, S.; Chénier, M.; Levesque, C.; Maclean, L.; Marro, L.; Jones-Otazo, H.; Petrovic, S.; McDonald, L.; Gardner, H., Canadian House Dust Study: Lead Bioaccessibility and Speciation. *Environmental Science & Technology* 2011, 45, (11), 4959.
- Reeder, R. J.; Schoonen, M. A. A.; Lanzirotti, A., Metal speciation and its role in bioaccessibility and bioavailability. *Reviews in Mineralogy and Geochemistry* 2006, 64, 59-113.
- Ruby, M.; Davis, A.; Nicholson, A., In situ formation of lead phosphates in soils as a method to immobilize lead. *Environmental Science & Technology* 1994, 28, (4), 646.
- Scheckel, K. G.; Diamond, G. L.; Burgess, M. F.; Klotzbach, J. M.; Maddaloni, M.; Miller, B. W.; Partridge, C. R.; Serda, S. M., Amending soils with phosphate as means to mitigate soil lead hazard: A critical review of the state of the science. *Journal of Toxicology and Environmental Health, Part B* 2013, 16, (6), 337-380.
- Schroth, A.; Bostick, B.; Kaste, J.; Friedland, A., Lead Sequestration and Species Redistribution During Soil Organic Matter Decomposition. *Environmental Science & Technology* 2008, 42, (10), 3627.
- Schwab, A. P.; Lewis, K.; Banks, M. K., Lead stabilization by phosphate amendments in soil impacted by paint residue. *Journal of environmental science and health. Part A, Toxic/Hazardous Substances & Environmental Engineering* 2006, 41, (3), 359.
- Schwertmann, U.; Cornell, R. M., Chemistry -- Iron Oxides in the Laboratory: Preparation and Characterization by U. Schwertmann and R. M. Cornell. In *American Library Association: Middletown*, 1992; Vol. 29, p 770.
- Shahid, M., Assessment of lead speciation by organic ligands using speciation models. *Chemical Speciation and Bioavailability* 2012, 24, (4), 248-252.
- Steefel, C.; Appelo, C.; Arora, B.; Jacques, D.; Kalbacher, T.; Kolditz, O.; Lagneau, V.; Lichtner, P.; Mayer, K.; Meeussen, J.; Molins, S.; Moulton, D.; Shao, H.; Simnek,

- J.; Spycher, N.; Yabusaki, S.; Yeh, G., Reactive transport codes for subsurface environmental simulation. *Computational Geosciences* 2015, 19, (3), 445-478.
- Walraven, N.; Bakker, M.; van Os, B. J. H.; Klaver, G. T.; Middelburg, J. J.; Davies, G. R., Factors controlling the oral bioaccessibility of anthropogenic Pb in polluted soils. *Science of the Total Environment* 2015, 506-507, 149-163.
- Wang, C.; Lazouskaya, V.; Fuller, M.; Caplan, J.; Schaefer, C.; Jin, Y., Dissolution of Microscale Energetic Residues in Saturated Porous Media: Visualization and Quantification at the Pore-Scale by Spectral Confocal Microscopy. *Environmental Science & Technology* 2011, 45, (19), 8352.
- Weber, J. S.; Goyne, K. W.; Luxton, T. P.; Thompson, A. L., Phosphate Treatment of Lead- Contaminated Soil: Effects on Water Quality, Plant Uptake, and Lead Speciation. *Journal of Environmental Quality* 2015, 44, (4), 1127.
- Zia, M. H.; Codling, E. E.; Scheckel, K. G.; Chaney, R. L., In vitro and in vivo approaches for the measurement of oral bioavailability of lead (Pb) in contaminated soils: a review. *Environmental Pollution* 2011, 159, (10), 2320.

3.5. Tables

Table 1. Rainwater preparations used for column experiments.

Solute	RW 1 (mmol L ⁻¹)	RW 2	RW 3	RW 4
NaHCO ₃	0.03	0.03	0.03	0.03
MgCl ₂ • 2H ₂ O	0.005	0.005	0.005	0.005
K ₂ SO ₄	0.004	0.004	0.004	0.004
NH ₄ NO ₃	0.04	0.04	0.04	0.04
CaCl ₂	0.01	0.01	0.01	0.01
MgSO ₄ • 7H ₂ O	0.005	0.005	0.005	0.005
H ₂ SO ₄	0.04	0.04	0.04	0.04
0.1 M 1H ₃ PO ₄	N/A	N/A	N/A	3.00
pH	3.00	4.00	5.00	3.00

Table 2. Column preparations and replicates.²

RW preparation	RW only	0.57 mg kg ⁻¹ FeOOH	1.14 mg kg ⁻¹ FeOOH	2.28 mg kg ⁻¹ FeOOH
1: No PO ₄ ; pH 3	• • •	N/A	N/A	N/A
2: No PO ₄ ; pH 4	•	N/A	N/A	N/A
3: No PO ₄ ; pH 5	•	N/A	N/A	N/A
4: PO ₄ ; pH 3	• • • •	• • •	• • • •	• •

² Each point symbol (•) represents a single column experiment, while N/A indicates no column experiment was conducted.

Table 3. Characteristics of soil selected for use in columns.

Particle	Bulk %	Mineral	Bulk %	Fine fraction %	Carbon (g g⁻¹)	Pb (mg kg⁻¹)
Sand	82.1	Quartz	67.4	14.6	0.0749	11250
Silt	16.7	Albite	18.6	37.0		
Clay	1.2	Chlorite	7.2	18.5		
		Goethite	6.2	8.1		
		Muscovite	0.6	21.9		

Table 4. Bioaccessibility of Pb in unleached soil and after column experiments.

Soil Preparation	Bioaccessible Fraction
Unleached soil	0.675±0.006
Column + RW without PO ₄	0.768±0.001
Column + RW + PO ₄	0.767±0.012
Column + RW + PO ₄ + 0.06% FeO(OH)	0.596±0.007
Column + RW + PO ₄ + 0.13% FeO(OH)	0.653±0.015

3.6 Figures

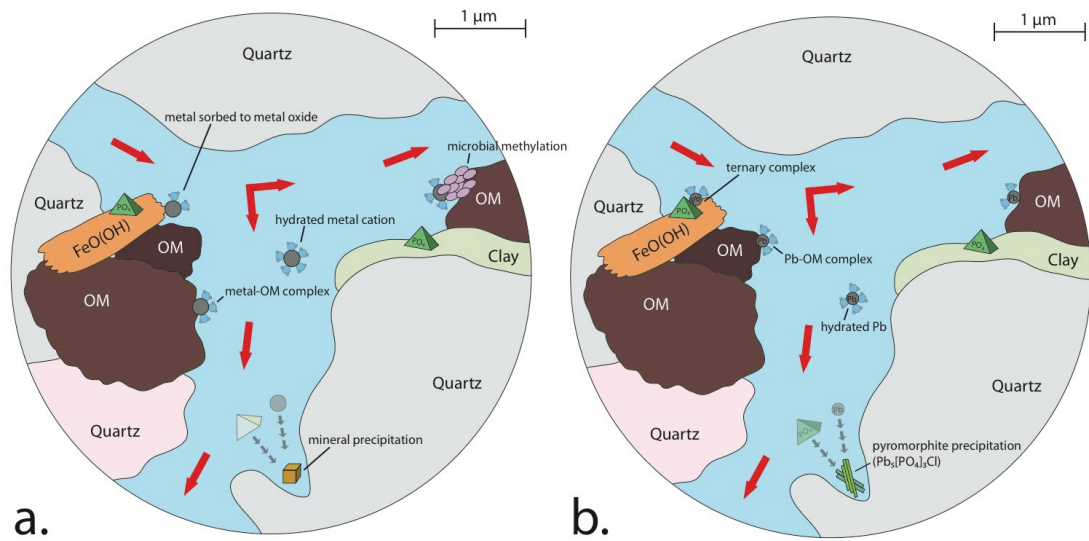


Figure 1. a. Representation of contaminant metal (gray sphere) behavior within soil microenvironments in an example soil pore space (quartz dominated). Red arrows represent flow direction. b. Specific behavior at soil microsites affecting Pb ions in solution.

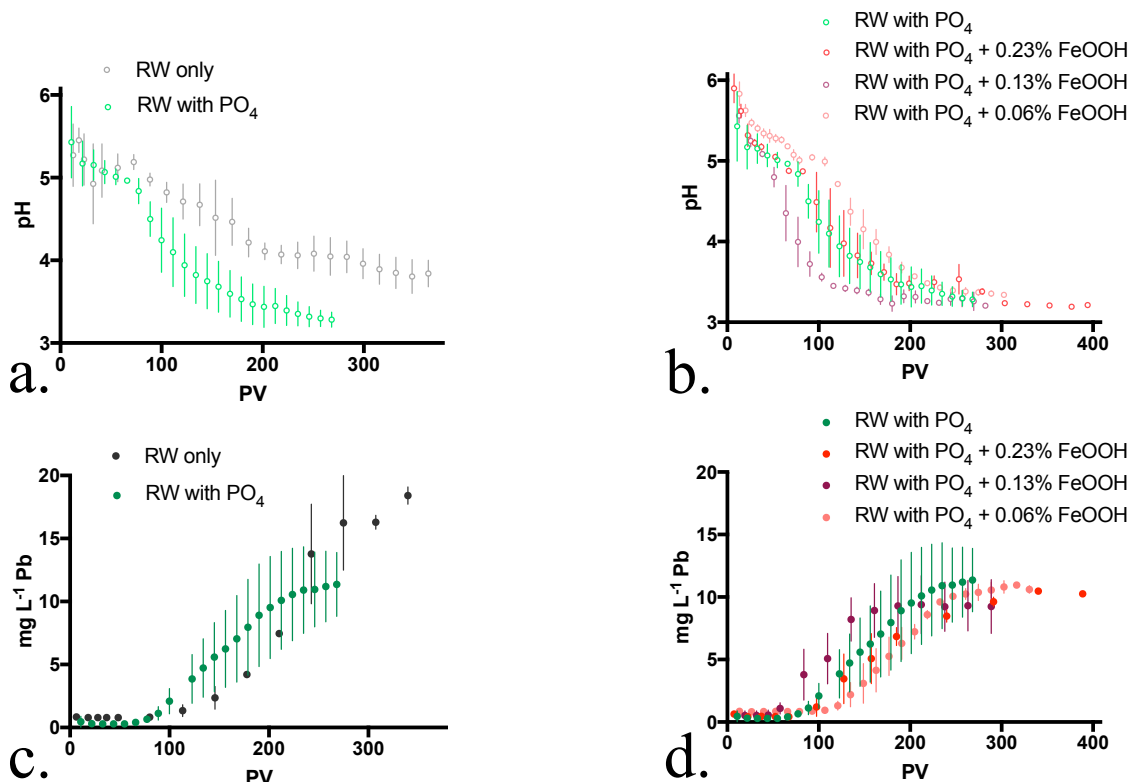


Figure 2. a (upper left). pH over time (PV = Pore Volume) within columns leached with acidified rainwater and acidified rainwater modified with PO_4 , respectively; both were conducted at pH of 3 and unamended with goethite. Figure 2b (lower left). Pb concentration over time within columns mentioned in 2a. Figure 2c (upper right). pH over time within columns leached with PO_4 and amended with various goethite ($\text{FeO}[\text{OH}]$) preparations, all conducted at pH of 3. Figure 2d (lower right). Pb concentration over time within columns mentioned in 2c.

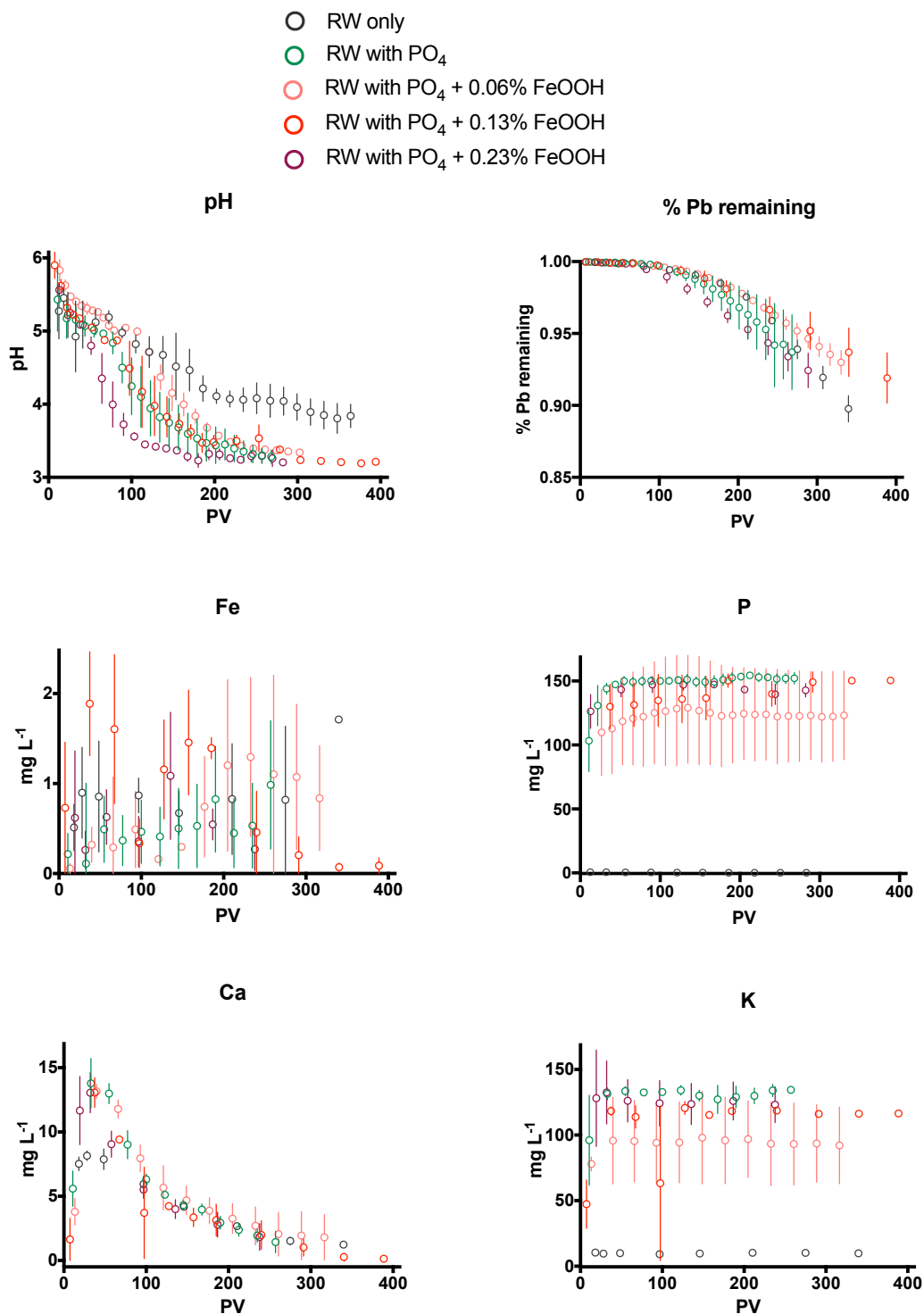


Figure 3. Concentration of various elements within column experiment effluent; Pb concentration is subtracted from total estimated Pb to give estimated fraction Pb remaining.

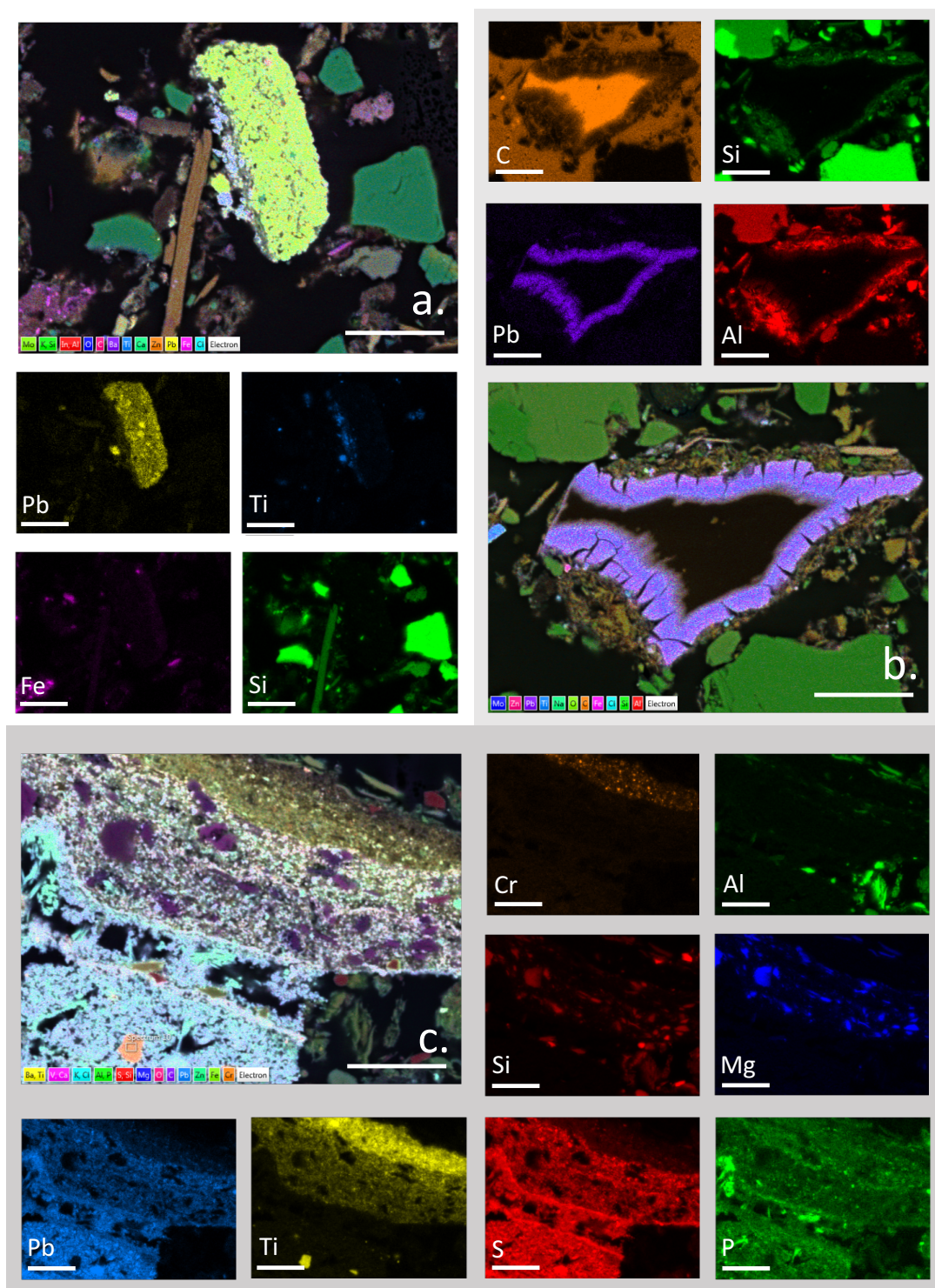


Figure 4. a, b. Microscale SEM-EDS images of soil particles within unleached column; c. Microscale SEM-EDS images of soil particles within column leached with PO₄-amended rainwater and amended with FeO(OH). Scale bar represents 50 μm.

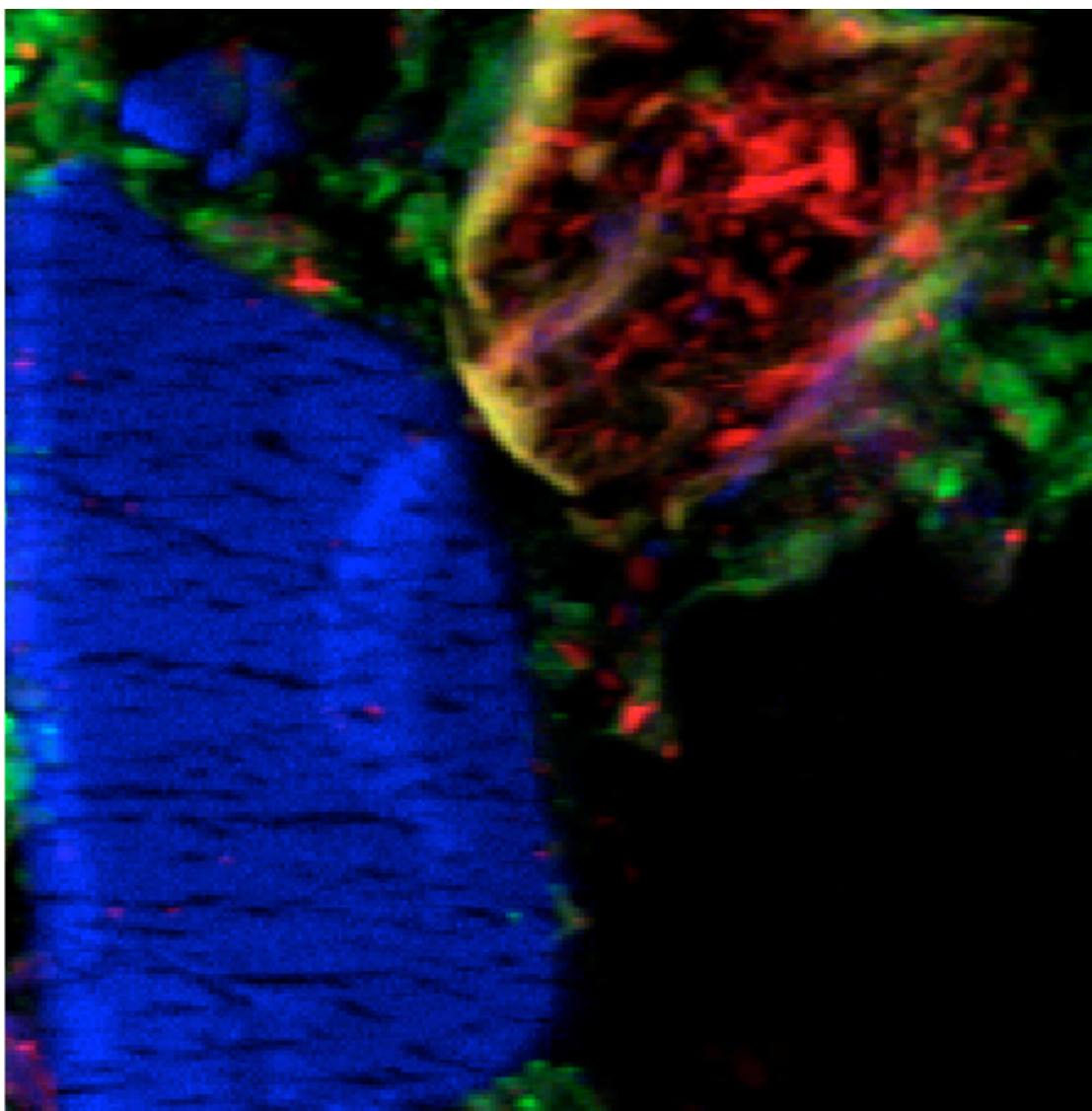


Figure 5. Combined μ XRF map, with Pb given in green, K in blue, and Fe in red, within column leached with PO_4 -amended rainwater.

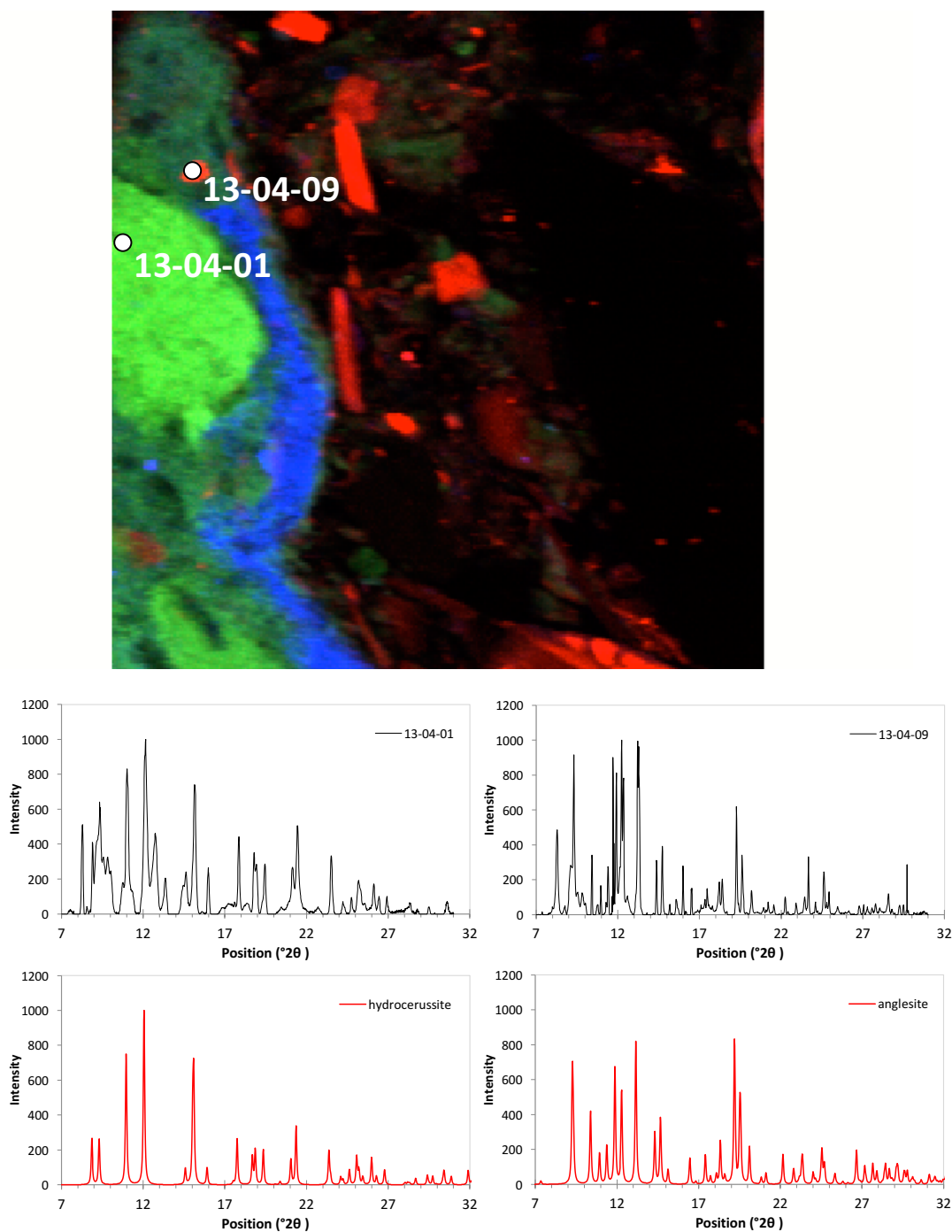


Figure 6. Top: Combined μ XRF map, with Pb given in green, Zn in blue, and Fe in red, within column leached with PO_4 -amended rainwater. Locations where significant μ XRD patterns of Pb minerals were collected are given by white dots and labeled with pattern number. Bottom: Comparisons between μ XRD pattern collected from sample (top pattern) and reference mineral (lower pattern) for samples 13-04-01 and 13-04-09.

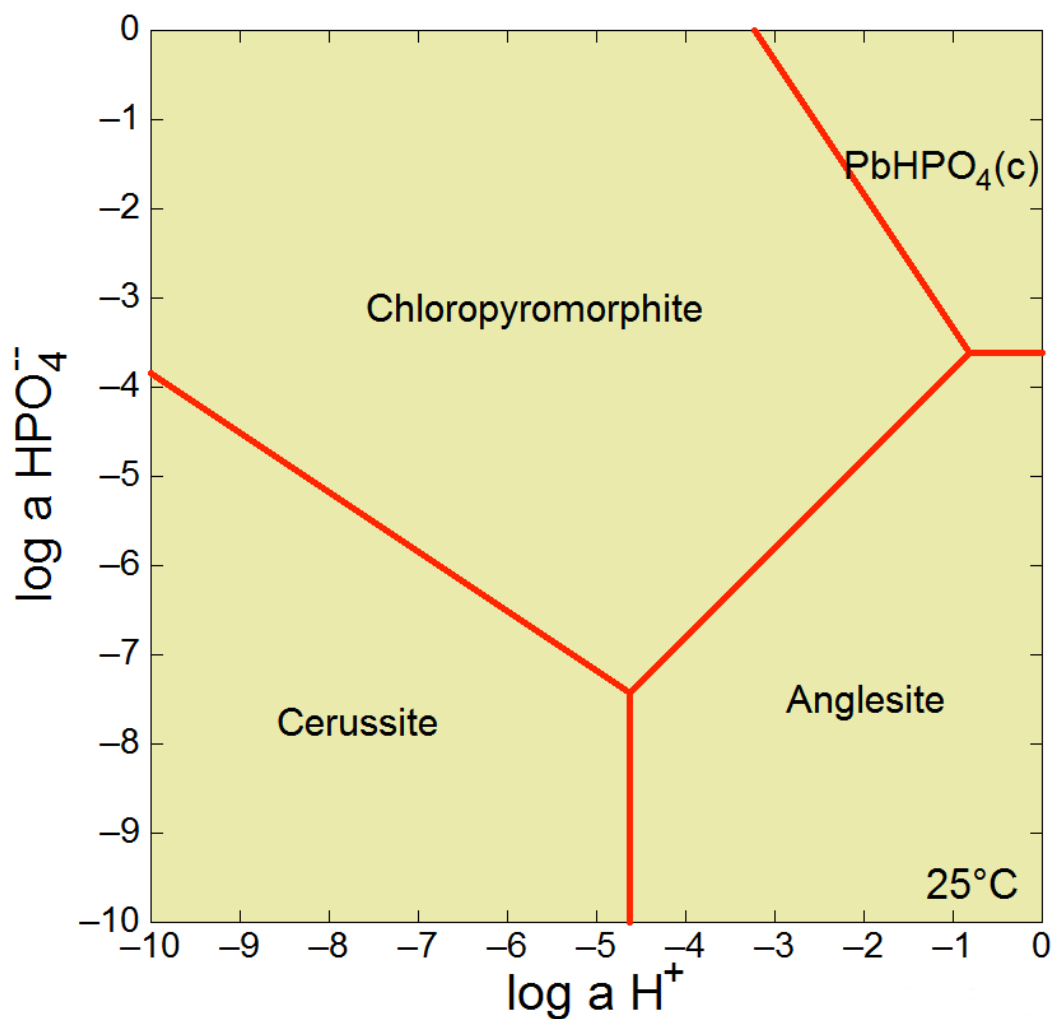


Figure 7. Diagram showing relative stability of PbCO_3 (cerussite) and derivative species (PbSO_4 [anglesite], $\text{Pb}_5\text{Pb}_3[\text{PO}_4]_3\text{Cl}$ [chloropyromorphite], and PbHPO_4 [lead hydrogen phosphate]) in an aqueous system in the presence of SO_4^{2-} , Fe^{2+} , HCO_3^- , and Cl^- , all ions with activities of 1.0, in response to changing pH and $\log \text{HPO}_4^{2-}$.

CHAPTER 4: Concluding Remarks and Future Work

The site-specific nature of this locally embedded work contributes to Burlington's history as a place and reinforces local knowledge regarding the contamination landscape of this area. Neighborhoods with the highest Pb concentrations, including the Old North End and Winooski (a city that is part of the greater Burlington area), have historically housed people of color, immigrants, and low income renters. The environmental burden faced by these marginalized communities has extended from Burlington's past as a city of industrial activity, when Italian, Irish, and Jewish immigrant communities worked in foundries and mills, to the present, with Somalian, Bhutanese, Vietnamese, and Nepali communities living in post-industrial areas affected by paint-related Pb contamination and in proximity to brownfields. By working with the Burlington Lead Program, a local nonprofit that offers services to residents in these worst-affected areas, and with the Governor's Institute of Vermont, a program that offers Vermont high schoolers local research experiences, our intent was to situate this work within a historical and community-based context. In the future, this data will be provided to the City of Burlington and the Vermont Department of Health to make this work more accessible and so that resources may be targeted to areas most affected. Meanwhile, our bank of Pb samples will continue to accumulate through the work of current and future students to further explore Pb dynamics locally using advanced techniques. Ideally, this study will be replicated within another soil type to verify the correlation between total and extractable Pb for a single soil so that site-specific thresholds may be derived for other areas and soil types. This will form a longstanding contribution to the study of site-

specific behavior of Pb and inform a place-based understanding of contaminant dynamics in complicated soil systems.

Future column experiments will use the framework of the second part of this study to examine the effects of discretization of competitive sorbents in stratified horizontal zones within columns. In addition, speciation information and results of effluent and solid phase analysis will be used to construct predictive speciation and transport models and examine effects of competitive behavior on wider scales to assist in the refinement of remediation techniques. There remains work to be done in studying the effect of reactive amorphous Fe oxides on the ability of PO_4 to immobilize Pb within near-field soil systems; future work could investigate the kinetics of Pb desorption from complex heterogeneous, iron-rich aggregates and organic matter clumps for binding to PO_4 .

This second part of this work offers implications that contradict the hypothesis that Pb is becoming less bioavailable over time within urban areas. In some urban residential areas, ground is prepared using fertilizer, introducing significant sources of PO_4 into the soil; however, many other urban areas consist of sparsely placed grass and eroding technosols containing a diverse mix of anthropogenic sediments, and may be depleted, rather than enriched in organic matter. Furthermore, even if PO_4 is added to soils, competitive dynamics may not lead it to bind preferentially with Pb; in fact, the alteration of Pb within this study from cerussite to the less soluble anglesite impeded formation of pyromorphite, and thus impeded the efficiency of remediation, since anglesite is stable at low pH (Figure 7) but is more bioaccessible with respect to pyromorphite (Chapter 1, Figure 2).

More work is needed to constrain and predict the behavior of accessory elements involved in the weathering of Pb paint; the interplay between Cr, Pb, Ti, Zn, Ba, and other paint constituents in competing for reactive sites could lead to complex changes in speciation and mobility (Christl and Kretzschmar, 1999; Flogeac et al., 2007; Merdy et al., 2009; Serrano et al., 2009), which implicate changes in bioavailability (Ollson et al., 2017). Furthermore, the effect of PO₄ remediation methods, and the soil acidification or EDTA applications currently used to increase efficacy, should be weighed against unexpected effects on the solubility of these accessory metals. For example, in areas affected by dual contributions of Pb and As from smelting, the application of PO₄ amendments to immobilize Pb has the side effect of increasing As mobility (Cui et al., 2010; Impellitteri, 2005). The presence of accessory paint elements in combination with Pb can also muddle efforts to measure the fate and transport of Pb within soils; Ti was used as an index element in the past to measure Pb mobility (Johnson et al., 2004), and urban Ti enrichment in top soil horizon from paint would impair its accuracy in this regard. Finally, Pb located on the underside of paint chips from more recent weathering events appears to exhibit more structural cohesiveness than Pb from earlier chalking events. This indicates that a distinction may be created between weathering patterns of Pb that has significant implications for speciation and mobility, with fine particles of Pb exhibiting a more rapid change in speciation, and likely being incorporated into aggregates and sorbing to organic matter and oxides, and paint chips constrained by morphological features, with Pb species altering within outer layers.

This study presents a framework for future efforts to undertake speciation and reactive transport modeling to study competitive dynamics related to Pb at a single site,

and offers potential for tailoring remediation methods to address Pb heterogeneity locally by using analysis of microscale soil dynamics and biogeochemistry to refine methods at the field scale.

CHAPTER 5: Comprehensive Reference List

- Alloway, B. J., Heavy Metals in Soils: Trace Metals and Metalloids in Soils and their Bioavailability. Springer Netherlands: 2012.
- Altomare, A.; Cuocci, C.; Giacobazzo, C.; Moliterni, A.; Rizzi, R., QUALX: a computer program for qualitative analysis using powder diffraction data. *Journal of Applied Crystallography* 2008, 41, (4), 815.
- An, J.; Jho, E. H.; Nam, K., Effect of dissolved humic acid on the Pb bioavailability in soil solution and its consequence on ecological risk. *Journal of Hazardous Materials* 2015, 286, 236-241.
- Attanayake, C. P.; Hettiarachchi, G. M.; Martin, S.; Pierzynski, G. M., Potential bioavailability of lead, arsenic, and polycyclic aromatic hydrocarbons in compost-amended urban soils. *Journal of Environmental Quality* 2015, 44, (3), 930.
- Baker, L.; Pierzynski, G.; Hettiarachchi, G.; Scheckel, K.; Newville, M., Micro- X- Ray Fluorescence, Micro- X- Ray Absorption Spectroscopy, and Micro- X- Ray Diffraction Investigation of Lead Speciation after the Addition of Different Phosphorus Amendments to a Smelter-Contaminated Soil. *Journal of Environmental Quality* 2014, 43, (2), 488-497.
- Bargar, J. R.; Brown, G. E.; Parks, G. A., Surface Complexation of Pb(II) at Oxide-Water Interfaces: III. XAFS Determination of Pb(II) and Pb(II)-Chloro Adsorption Complexes on Goethite and Alumina. *Geochimica et Cosmochimica Acta* 1998, 62, (2), 193-207.
- Blaylock, M. J.; Salt, D. E.; Dushenkov, S.; Zakharova, O.; Gussman, C.; Kapulnik, Y.; Ensley, B. D.; Raskin, I., Enhanced accumulation of Pb in Indian mustard by soil-applied chelating agents. *Environmental Science & Technology* 1997, 31, (3), 860.
- Bolan, N.; Kunhikrishnan, A.; Thangarajan, R.; Kumpiene, J.; Park, J.; Makino, T.; Kirkham, M. B.; Scheckel, K., Remediation of heavy metal(loid)s contaminated soils – To mobilize or to immobilize? *Journal of Hazardous Materials* 2014, 266, 141-166.
- Brown, S.; Chaney, R.; Hallfrisch, J.; Ryan, J. A.; Berti, W. R., In situ soil treatments to reduce the phyto- and bioavailability of lead, zinc, and cadmium. *Journal of Environmental Quality* 2004, 33, (2), 522-531.
- Burt, R.; Hernandez, L.; Shaw, R.; Tunstead, R.; Ferguson, R.; Peaslee, S., Trace element concentration and speciation in selected urban soils in New York City. *Environmental Monitoring and Assessment* 2014, 186, (1), 195-215.

- Cancès, B.; Ponthieu, M.; Castrec-Rouelle, M.; Aubry, E.; Benedetti, M. F., Metal ions speciation in a soil and its solution: experimental data and model results. *Geoderma* 2003, 113, (3), 341-355.
- Cao, X.; Ma, L. Q.; Chen, M.; Hardison, D. W.; Harris, W. G., Weathering of lead bullets and their environmental effects at outdoor shooting ranges. *Journal of Environmental Quality* 2003, 32, (2), 526.
- Cao, X.; Ma, L. Q.; Chen, M.; Singh, S. P.; Harris, W. G., Impacts of phosphate amendments on lead biogeochemistry at a contaminated site. *Environmental science & technology* 2002, 36, (24), 5296.
- Cattle, J.; McBratney, A. B.; Minasny, B., Kriging method evaluation for assessing the spatial distribution of urban soil lead contamination. *Journal of Environmental Quality* 2002, 31, (5), 1576-1588.
- CDC, Low Level Lead Exposure Harms Children: A Renewed Call for Primary Prevention: Report of the Advisory ommittee on Childhood Lead Poisoning Prevention of the Centers for Disease Control and Prevention. 2012.
- Chaney, R. L.; Mielke, H. W.; Sterrett, S. B., Speciation, mobility and bioavailability of soil lead. *Environmental Geochemistry and Health* 1989, (11), 105-129.
- Chorover, J.; Amistadi, M. K., Reaction of forest floor organic matter at goethite, birnessite and smectite surfaces. *Geochimica et Cosmochimica Acta* 2001, 65, (1), 95-109.
- Christl, I.; Kretzschmar, R., Competitive sorption of copper and lead at the oxide- water interface: Implications for surface site density. *Geochimica Et Cosmochimica Acta* 1999, 63, (19-20), 2929-2938.
- Chrysochoou, M.; Dermatas, D.; Grubb, D. G., Phosphate application to firing range soils for Pb immobilization: The unclear role of phosphate. *Journal of Hazardous Materials* 2007, 144, (1), 1-14.
- Clark, H. F.; Hausladen, D. M.; Brabander, D. J., Urban gardens: Lead exposure, recontamination mechanisms, and implications for remediation design. *Environmental Research* 2008, 107, (3), 312-319.
- Clark, J. J.; Knudsen, A. C., Extent, characterization, and sources of soil lead contamination in small-urban residential neighborhoods. *Journal of Environmental Quality* 2013, 42, (5), 1498-1506.
- Cotter-Howells, J.; Caporn, S., Remediation of contaminated land by formation of heavy metal phosphates. *Applied Geochemistry* 1996, 11, (1), 335-342.

- Cui, Y.; Du, X.; Weng, L.; Van Riemsdijk, W. H., Assessment of in situ immobilization of lead (Pb) and arsenic (As) in contaminated soils with phosphate and iron: solubility and bioaccessibility. *Water, Air, & Soil Pollution* 2010, 213, (1-4), 95.
- Davis, A. P.; Burns, M., Evaluation of lead concentration in runoff from painted structures. *Water Research* 1999, 33, (13), 2949-2958.
- Davis, A.; Drexler, J.; Ruby, M.; Nicholson, A., Micromineralogy of mine wastes in relation to lead bioavailability, Butte, Montana. *Environmental Science & Technology* 1993, 27, (7), 1415.
- Davis, A.; Ruby, M.; Bergstrom, P., Bioavailability of arsenic and lead in soils from the Butte, Montana, mining district. *Environmental Science & Technology* 1992, 26, (3), 461.
- de Miguel, E.; Mingot, J.; Chacón, E.; Charlesworth, S., The relationship between soil geochemistry and the bioaccessibility of trace elements in playground soil. *Environmental Geochemistry and Health* 2012, 34, (6), 677-687.
- Debela, F.; Arocena, J.; Thring, R. W.; Whitcombe, T., Organic acids inhibit the formation of pyromorphite and Zn-phosphate in phosphorous amended Pb- and Zn-contaminated soil. *Journal of Environmental Management* 2013, 116, 156.
- Deshommes, E.; Tardif, R.; Edwards, M.; Sauvé, S.; Prévost, M., Experimental determination of the oral bioavailability and bioaccessibility of lead particles. *Chemistry Central Journal* 2012, 6, (1), 138.
- Despart, Z., Burlington considers prosecuting landlord. *Burlington Free Press* 2015.
- Dickinson, N.; Baker, A.; Doronila, A.; Laidlaw, S.; Reeves, R., Phytoremediation of inorganics: realism and synergies. *International Journal of Phytoremediation* 2009, 11, (2), 97.
- Drexler, J.; Brattin, W., An In Vitro Procedure for Estimation of Lead Relative Bioavailability: With Validation. *Human and Ecological Risk Assessment* 2007, 13, (2), 383-401.
- Edwards, R.; Lam, N.; Zhang, L.; Johnson, M.; Kleinman, M., Nitrogen Dioxide and Ozone As Factors in the Availability of Lead from Lead- Based Paints. *Environmental Science & Technology* 2009, 43, (22), 8516.
- Elemental Microanalysis Limited, Certificate of Analysis: Low Organic Content Soil OAS. In CatNo B2152 - Certificate No. 207835, Devon, England, 2016.
- EPA IEUBK Model Bioavailability Variable (short sheet); 1999.
- EPA, In Vitro Bioaccessibility Assay for Lead in Soil. SW-846 2013, (1340), 24.

- EPA, Sources of Lead in Soil: A Literature Review, EPA 747-R-98-001a. National Center for Environmental Assessment, US Environmental Protection Agency, Washington, D.C. 1998.
- Esler, D., Getting the lead out: the future of avgas.(unleaded aviation gasoline)(Operations). *Business & Commercial Aviation* 2015, 111, (2), 30.
- Filippelli, G. M.; Laidlaw, M. A. S.; Latimer, J. C.; Raftis, R., Urban lead poisoning and medical geology: An unfinished story. *GSA Today* 2005, 15, (1), 4-11.
- Filippelli, G.; Laidlaw, M., THE ELEPHANT IN THE PLAYGROUND confronting lead- contaminated soils as an important source of lead burdens to urban populations. *Perspectives In Biology And Medicine* 2010, 53, (1), 31-45.
- Flogeac, K.; Guillon, E.; Aplincourt, M., Competitive sorption of metal ions onto a north-eastern France soil. Isotherms and XAFS studies. *Geoderma* 2007, 139, (1), 180-189.
- Ford, R.; Bertsch, P.; Farley, K., Changes in transition and heavy metal partitioning during hydrous iron oxide aging. *Environmental Science & Technology* 1997, 31, (7), 2028-2033.
- Glorennec, P.; Declercq, C., Performance of several decision support tools for determining the need for systematic screening of childhood lead poisoning around industrial sites. *European Journal of Public Health* 2007, 17, (1), 47-52.
- Glorennec, P.; Peyr, C.; Poupon, J.; Oulhote, Y.; Le Bot, B., Identifying sources of lead exposure for children, with lead concentrations and isotope ratios. *Journal of Occupational and Environmental Hygiene* 2010, 7, (5), 253.
- Goovaerts, P., Geostatistics in soil science: state-of-the-art and perspectives. *Geoderma* 1999, 89, (1), 1-45.
- Gražulis, S.; Chateigner, D.; Downs, R. T.; Yokochi, A. F. T.; Quirós, M.; Lutterotti, L.; Manakova, E.; Butkus, J.; Moeck, P.; Le Bail, A., Crystallography Open Database – an open- access collection of crystal structures. *Journal of Applied Crystallography* 2009, 42, (4), 726-729.
- Ha, H.; Olson, J.; Bian, L.; Rogerson, P., Analysis of Heavy Metal Sources in Soil Using Kriging Interpolation on Principal Components. *Environmental Science & Technology* 2014, 48, (9), 4999.
- Hashimoto, Y.; Takaoka, M.; Oshita, K.; Tanida, H., Incomplete transformations of Pb to pyromorphite by phosphate-induced immobilization investigated by X-ray absorption fine structure (XAFS) spectroscopy. *Chemosphere* 2009, 76, (5), 616.

- Hashimoto, Y.; Takaoka, M.; Shiota, K., Enhanced Transformation of Lead Speciation in Rhizosphere Soils Using Phosphorus Amendments and Phytostabilization: An X-ray Absorption Fine Structure Spectroscopy Investigation. *Journal of Environmental Quality* 2011, 40, (3), 696-703.
- Hashimoto, Y.; Yamaguchi, N.; Takaoka, M.; Shiota, K., EXAFS speciation and phytoavailability of Pb in a contaminated soil amended with compost and gypsum. *Science of the Total Environment* 2011, 409, (5), 1001-1007.
- Hemphill, C. P.; Ruby, M. V.; Beck, B. D.; Davis, A.; Bergstrom, P. D., The bioavailability of lead in mining wastes: physical/chemical considerations. *Chemical Speciation & Bioavailability* 1991, 3, (3-4), 135-148.
- Henry, H.; Naujokas, M.; Attanayake, C.; Basta, N.; Cheng, Z.; Hettiarachchi, G.; Maddaloni, M.; Schadt, C.; Scheckel, K., Bioavailability- Based In Situ Remediation To Meet Future Lead (Pb) Standards in Urban Soils and Gardens. *Environmental Science & Technology* 2015, 49, (15), 8948.
- Hesterberg, D.; Duff, M.; Dixon, J.; Vepraskas, M., X- ray Microspectroscopy and Chemical Reactions in Soil Microsites. *Journal of Environmental Quality* 2011, 40, (3), 667-78.
- Hettiarachchi, G. M.; Pierzynski, G. M., Soil lead bioavailability and in situ remediation of lead- contaminated soils: A review. *Environmental Progress* 2004, 23, (1), 78-93.
- Hettiarachchi, G.; Pierzynski, G.; Oehme, F.; Sonmez, O.; Ryan, J., Treatment of contaminated soil with phosphorus and manganese oxide reduces lead absorption by Sprague-Dawley rats. *Journal of Environmental Quality* 2003, 32, (4), 1335-45.
- Hettiarachchi, G.; Pierzynski, G.; Ransom, M., In situ stabilization of soil lead using phosphorus and manganese oxide. *Environmental Science & Technology* 2000, 34, (21), 4614-4619.
- Hiemstra, T.; Mia, S.; Duhaut, P.-B.; Molleman, B., Natural and Pyrogenic Humic Acids at Goethite and Natural Oxide Surfaces Interacting with Phosphate. *Environmental Science & Technology* 2013, 47, (16), 9182.
- Hodson, M. E., The Need for Sustainable Soil Remediation. *Elements* 2010, 6, (6), 363-368.
- Hong, S.; Candelone, J.-P.; Patterson, C. C.; Boutron, C. F., Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations. *Science* 1994, 265, (5180), 1841.

- Hopwood, J. D.; Davey, R. J.; Jones, M. O.; Pritchard, R. G.; Cardew, P. T.; Booth, A., Development of chloropyromorphite coatings for lead water pipes. *Journal of Materials Chemistry* 2002, 12, (6), 1717-1723.
- Hunt, A., Relative bioaccessibility of Pb-based paint in soil. *Environmental geochemistry and health* 2016, 38, (4), 1037.
- Impellitteri, C. A., Effects of pH and phosphate on metal distribution with emphasis on As speciation and mobilization in soils from a lead smelting site. *The Science of the Total Environment* 2005, 345, (1-3), 175.
- Jackson, B.; Williams, P.; Lanzirrotti, A.; Bertsch, P., Evidence for Biogenic Pyromorphite Formation by the Nematode *Caenorhabditis elegans*. *Environmental Science & Technology* 2005, 39, (15), 5620-5625.
- Jacobs, D. E.; Clickner, R. P.; Zhou, J. Y.; Viet, S. M.; Marker, D. A.; Rogers, J. W.; Zeldin, D. C.; Broene, P.; Friedman, W., The prevalence of lead-based paint hazards in U.S. housing. *Environmental Health Perspectives* 2002, 110, (10), A599.
- Johnson, C. C.; Demetriades, A.; Locutura, J.; Ottesen, R. T., Mapping the Chemical Environment of Urban Areas. Wiley: 2011.
- Johnson, C.; Petras, R.; April, R.; Siccama, T., Post-Glacial Lead Dynamics in a Forest Soil. *Water, Air, & Soil Pollution: Focus* 2004, 4, (2), 579-590.
- Juhasz, A.; Gancarz, D.; Herde, C.; McClure, S.; Scheckel, K.; Smith, E., In Situ Formation of Pyromorphite Is Not Required for the Reduction of in Vivo Pb Relative Bioavailability in Contaminated Soils. *Environmental Science & Technology* 2014, 48, (12), 7002.
- Kaste, J., Tracing the retention and redistribution of lead and other atmospheric fallout in soils. In Friedland, A. J., Ed. ProQuest Dissertations Publishing: 2003.
- Kaste, J.; Bostick, B.; Friedland, A.; Schroth, A.; Siccama, T., Fate and Speciation of Gasoline- Derived Lead in Organic Horizons of the Northeastern USA. *Soil Science Society of America Journal* 2006, 70, (5), 1688-1698.
- Kim, D.; Staley, F.; Curtis, G.; Buchanan, S., Relation between housing age, housing value, and childhood blood lead levels in children in Jefferson County, Ky. *American Journal of Public Health* 2002, 92, (5), 769-72.
- Kirpichtchikova, T. A.; Manceau, A.; Spadini, L.; Panfili, F.; Marcus, M. A.; Jacquet, T., Speciation and solubility of heavy metals in contaminated soil using X-ray microfluorescence, EXAFS spectroscopy, chemical extraction, and thermodynamic modeling. *Geochimica et Cosmochimica Acta* 2006, 70, (9), 2163.

- Kumpiene, J.; Lagerkvist, A.; Maurice, C., Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments--a review. *Waste management* (New York, N.Y.) 2008, 28, (1), 215.
- Laidlaw, M. A. S.; Filippelli, G. M., Resuspension of urban soils as a persistent source of lead poisoning in children: A review and new directions. *Applied Geochemistry* 2008, 23, (8), 2021-2039.
- Laidlaw, M. A. S.; Taylor, M. P., Potential for childhood lead poisoning in the inner cities of Australia due to exposure to lead in soil dust. *Environmental Pollution* 2011, 159, (1), 1-9.
- Laidlaw, M.; Filippelli, G.; Sadler, R.; Gonzales, C.; Ball, A.; Mielke, H., Children's Blood Lead Seasonality in Flint, Michigan (USA), and Soil-Sourced Lead Hazard Risks. *International Journal of Environmental Research and Public Health* 2016, 13, (4), 1-13.
- Lande, J., Area Diffraction Machine v1.0.4. 2013.
- Lanphear, B.; Burgoon, D.; Rust, S.; Eberly, S.; Galke, W., Environmental exposures to lead and urban children's blood lead levels. *Environmental Research* 1998, 76, (2), 120-130.
- Laxen, D. P. H.; Harrison, R. M., The highway as a source of water pollution: An appraisal with the heavy metal lead. *Water Research* 1977, 11, (1), 1-11.
- Linker, B.; Khatiwada, R.; Perdrial, N.; Abrell, L.; Sierra-Alvarez, R.; Field, J.; Chorover, J., Adsorption of novel insensitive munitions compounds at clay mineral and metal oxide surfaces. *Environmental Chemistry* 2015, 12, (1), 74-84.
- Linton, R. W.; Natusch, D. F. S.; Solomon, R. L.; Evans, C. A., Physicochemical characterization of lead in urban dusts. A microanalytical approach to lead tracing. *Environmental Science & Technology* 1980, 14, (2), 159-164.
- Manceau, A.; Boisset, M.-C.; Sarret, G.; Hazemann, J.-L.; Mench, M.; Cambier, P.; Prost, R., Direct determination of lead speciation in contaminated soils by EXAFS spectroscopy. *Environmental Science & Technology* 1996, 30, (5), 1540.
- Markus, J.; McBratney, A. B., A review of the contamination of soil with lead. *Environment International* 2001, 27, (5), 399-411.
- Martinez, C.; McBride, M., Dissolved and labile concentrations of Cd, Cu, Pb, and Zn in aged ferrihydrite-organic matter systems. *Environmental Science & Technology* 1999, 33, (5), 745-750.

- Marx, S. K.; Rashid, S.; Stromsoe, N., Global-scale patterns in anthropogenic Pb contamination reconstructed from natural archives. *Environmental Pollution* 2016, 213, 283-298.
- McClintock, N., A critical physical geography of urban soil contamination. *Geoforum* 2015, 65, 69-85.
- McGrath, D.; Zhang, C.; Carton, O. T., Geostatistical analyses and hazard assessment on soil lead in Silvermines area, Ireland. *Environmental Pollution* 2004, 127, (2), 239-248.
- Merdy, P.; Gharbi, L. T.; Lucas, Y., Pb, Cu and Cr interactions with soil: Sorption experiments and modelling. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2009, 347, (1 3), 192.
- Mielke, H. W.; Dugas, D.; Mielke, P. W.; Smith, K. S.; Gonzales, C. R., Associations between soil lead and childhood blood lead in urban New Orleans and rural Lafourche Parish of Louisiana. *Environmental Health Perspectives* 1997, 105, (9), 950.
- Mielke, H. W.; Reagan, P. L., Soil is an important pathway of human lead exposure. *Environmental Health Perspectives* 1998, 106, (Suppl 1), 217-229.
- Mielke, H.; Gonzales, C. R.; Mielke, P., The continuing impact of lead dust on children's blood lead: Comparison of public and private properties in New Orleans. *Environmental Research* 2011, 111, (8), 1164-1172.
- Mielke, H.; Gonzales, C. R.; Powell, E.; Mielke, P., Environmental and health disparities in residential communities of New Orleans: The need for soil lead intervention to advance primary prevention. *Environment International* 2013, 51, 73-81.
- Miranda, M.; Anthopolos, R.; Hastings, D., A Geospatial Analysis of the Effects of Aviation Gasoline on Childhood Blood Lead Levels. *Environmental Health Perspectives* 2011, 119, (10), 1513-1516.
- Miretzky, P.; Fernandez-Cirelli, A., Phosphates for Pb immobilization in soils: a review. *Environ Chem Lett* 2008, 6, (3), 121-133.
- Morin, G.; Ostergren, J. D.; Juillot, F.; Ildefonse, P.; Calas, G.; Brown, G. E., Jr., XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: Importance of adsorption processes. *American Mineralogist* 1999, 420.
- Morrison, D.; Lin, Q.; Wiehe, S.; Liu, G.; Rosenman, M.; Fuller, T.; Wang, J.; Filippelli, G., Spatial relationships between lead sources and children's blood lead levels in the urban center of Indianapolis (USA). *Environmental Geochemistry And Health* 2013, 35, (2), 171-183.

- Moukana, J.; Asaue, H.; Koike, K., Co-kriging for modeling shallow groundwater level changes in consideration of land use/land cover pattern. *Environmental Earth Sciences* 2013, 70, (4), 1495-1506.
- Murozumi, M.; Chow, T. J.; Patterson, C., Chemical concentrations of pollutant lead aerosols, terrestrial dusts and sea salts in Greenland and Antarctic snow strata. *Geochimica et Cosmochimica Acta* 1969, 33, (10), 1247-1294.
- Negra, C.; Ross, D.; Lanzirotti, A., Soil manganese oxides and trace metals: competitive sorption and microfocused synchrotron x-ray fluorescence mapping. *J. Mol. Biol.* 2005, 330.
- Newville, M., Larch: An Analysis Package for XAFS and Related Spectroscopies. *J. Phys.: Conf. Ser.* 2013, 430, 012007.
- Newville, M.; Sutton, S. R.; Rivers, M. L.; Eng, P., Micro- beam X- ray absorption and fluorescence spectroscopies at GSECARS: APS beamline 13ID. *J Synchrotron Rad* 1999, 6, (3), 353-355.
- NIST, Certificate of Analysis: Standard Reference Material 2780. In *Hard Rock Mine Waste*, National Institute of Standards & Technology: Gaithersburg, MD, 2012; p 4.
- Nriagu, J. O., Lead orthophosphates—II. Stability of chlopyromophite at 25°C. *Geochimica et Cosmochimica Acta* 1973, 37, (3), 367-377.
- Nriagu, J. O., Lead orthophosphates—IV Formation and stability in the environment. *Geochimica et Cosmochimica Acta* 1974, 38, (6), 887-898.
- Nriagu, J. O., Saturnine gout among Roman aristocrats. Did lead poisoning contribute to the fall of the Empire? *The New England journal of medicine* 1983, 308, (11), 660.
- Obrycki, J. F.; Basta, N. T.; Scheckel, K.; Stevens, B. N.; Minca, K. K., Phosphorus Amendment Efficacy for In Situ Remediation of Soil Lead Depends on the Bioaccessible Method. *Journal of Environmental Quality* 2016, 45, (1), 37.
- Ollson, C. J.; Smith, E.; Herde, P.; Juhasz, A. L., Influence of co-contaminant exposure on the absorption of arsenic, cadmium and lead. *Chemosphere* 2017, 168, 658-666.
- Ostergren, J.; Brwn, G.; Parks, G.; Tingle, T., Quantitative speciation of lead in selected mine tailings from Leadville, CO. *Environmental Science & Technology* 1999, 33, (10), 1627-1636.
- Oulhote, Y.; Bot, B.; Poupon, J.; Lucas, J.-P.; Mandin, C.; Etchevers, A.; Zmirou-Navier, D.; Glorennec, P., Identification of sources of lead exposure in French children by

- lead isotope analysis: a cross-sectional study. *Environmental Health* 2011, 10, (1), 75.
- Palmer, S.; McIlwaine, R.; Ofterdinger, U.; Cox, S. F.; McKinley, J. M.; Doherty, R.; Wragg, J.; Cave, M., The effects of lead sources on oral bioaccessibility in soil and implications for contaminated land risk management. *Environmental Pollution* 2015, 198, 161-171.
- Park, J. H.; Lamb, D.; Paneerselvam, P.; Choppala, G.; Bolan, N.; Chung, J.-W., Role of organic amendments on enhanced bioremediation of heavy metal(loid) contaminated soils. *Journal of Hazardous Materials* 2011, 185, (2), 549-574.
- Perdrial, N.; Liewig, N.; Delphin, J.-E.; Elsass, F., TEM evidence for intracellular accumulation of lead by bacteria in subsurface environments. *Chemical Geology* 2008, 253, (3), 196-204.
- Perdrial, N.; Perdrial, J. N.; Delphin, J. E.; Elsass, F.; Liewig, N., Temporal and spatial monitoring of mobile nanoparticles in a vineyard soil: evidence of nanoaggregate formation. *European Journal of Soil Science* 2010, 61, (4), 456.
- Perdrial, N.; Thompson, A.; O'day, P. A.; Steefel, C. I.; Chorover, J., Mineral transformation controls speciation and pore- fluid transmission of contaminants in waste- weathered Hanford sediments. *Geochimica et Cosmochimica Acta* 2014, 141, 487-507.
- Peterson, J., Pb: Advances in Research on Effects of Lead on Children's Behavior and Intelligence. *Ambio* 1979, 8, (5), 223-226.
- Porter, S.; Scheckel, K.; Impellitteri, C.; Ryan, J., Toxic Metals in the Environment: Thermodynamic Considerations for Possible Immobilization Strategies for Pb, Cd, As, and Hg. *Critical Reviews in Environmental Science and Technology* 2004, 34, (6), 495-604.
- Rasmussen, P.; Beauchemin, S.; Chénier, M.; Levesque, C.; Maclean, L.; Marro, L.; Jones-Otazo, H.; Petrovic, S.; McDonald, L.; Gardner, H., Canadian House Dust Study: Lead Bioaccessibility and Speciation. *Environmental Science & Technology* 2011, 45, (11), 4959.
- Ratcliffe, N. M., Stanley, R.S., Gale, M.H., Thompson, P.J., and Walsh, G.J., Bedrock geologic map of Vermont. 2011, (U.S. Geological Survey Scientific Investigations Map 3184, 3 sheets, scale 1:100,000).
- Reeder, R. J.; Schoonen, M. A. A.; Lanzirrotti, A., Metal speciation and its role in bioaccessibility and bioavailability. *Reviews in Mineralogy and Geochemistry* 2006, 64, 59-113.

- Robinson, T. P.; Metternicht, G., Testing the performance of spatial interpolation techniques for mapping soil properties. *Computers and Electronics in Agriculture* 2006, 50, (2), 97-108.
- Rooney, C. P.; McLaren, R. G.; Condon, L., Control of lead solubility in soil contaminated with lead shot: Effect of soil pH. *Environmental Pollution* 2007, 149, (2), 149-157.
- Ruby, M.; Davis, A.; Kempton, J.; Drexler, J.; Bergstrom, P., Lead bioavailability: Dissolution kinetics under simulated gastric conditions. *Environmental Science & Technology* 1992, 26, (6), 1242.
- Ruby, M.; Davis, A.; Nicholson, A., In situ formation of lead phosphates in soils as a method to immobilize lead. *Environmental Science & Technology* 1994, 28, (4), 646.
- Ruby, M.; Schoof, R.; Brattin, W.; Goldade, M., Advances in evaluating the oral bioavailability of inorganics in soil for use in human health risk assessment. *Environmental Science & Technology* 1999, 33, (21), 3697-3705.
- Saby, N.; Arrouays, D.; Boulonne, L.; Jolivet, C.; Pochot, A., Geostatistical assessment of Pb in soil around Paris, France. *The Science of the Total Environment* 2006, 367, (1), 212.
- Sauve, S.; Martinez, C.; McBride, M.; Hendershot, W., Adsorption of free lead (Pb²⁺) by pedogenic oxides, ferrihydrite, and leaf compost. *Soil Science Society of America Journal* 2000, 64, (2), 595-599.
- Scheckel, K. G.; Diamond, G. L.; Burgess, M. F.; Klotzbach, J. M.; Maddaloni, M.; Miller, B. W.; Partridge, C. R.; Serda, S. M., Amending soils with phosphate as means to mitigate soil lead hazard: A critical review of the state of the science. *Journal of Toxicology and Environmental Health, Part B* 2013, 16, (6), 337-380.
- Scheckel, K.; Ryan, J., Spectroscopic Speciation and Quantification of Lead in Phosphate-Amended Soils. *Journal of Environmental Quality* 2004, 33, (4), 1288-95.
- Schroth, A.; Bostick, B.; Kaste, J.; Friedland, A., Lead Sequestration and Species Redistribution During Soil Organic Matter Decomposition. *Environmental Science & Technology* 2008, 42, (10), 3627.
- Schwab, A. P.; Lewis, K.; Banks, M. K., Lead stabilization by phosphate amendments in soil impacted by paint residue. *Journal of Environmental Science and Health*. 2006, 41, (3), 359.

- Schwarz, K.; Pickett, S. T. A.; Lathrop, R. G.; Weathers, K. C.; Pouyat, R. V.; Cadenasso, M. L., The effects of the urban built environment on the spatial distribution of lead in residential soils. *Environmental Pollution* 2012, 163, 32-39.
- Schwarz, K.; Weathers, K.; Pickett, S.; Lathrop, R.; Pouyat, R.; Cadenasso, M., A comparison of three empirically based, spatially explicit predictive models of residential soil Pb concentrations in Baltimore, Maryland, USA: understanding the variability within cities. *Environmental Geochemistry and Health* 2013, 35, (4), 495-510.
- Schwertmann, U.; Cornell, R. M., Chemistry -- Iron Oxides in the Laboratory: Preparation and Characterization by U. Schwertmann and R. M. Cornell. In *American Library Association dba CHOICE: Middletown*, 1992; Vol. 29, p 770.
- Semlali, R. M.; van Oort, F.; Denaix, L.; Loubet, M., Estimating distributions of endogenous and exogenous Pb in soils by using Pb isotopic ratios. *Environmental Science & Technology* 2001, 35, (21), 4180.
- Serrano, S.; O'day, P. A.; Vlassopoulos, D.; García-González, M. T.; Garrido, F., A surface complexation and ion exchange model of Pb and Cd competitive sorption on natural soils. *Geochimica et Cosmochimica Acta* 2009, 73, (3), 543-558.
- Settle, D. M.; Patterson, C. C., Lead in albacore: guide to lead pollution in Americans. *Science* 1980, 207, 1167.
- Shahid, M., Assessment of lead speciation by organic ligands using speciation models. *Chemical Speciation and Bioavailability* 2012, 24, (4), 248-252.
- Shahid, M.; Pinelli, E.; Dumat, C., Review of Pb availability and toxicity to plants in relation with metal speciation; role of synthetic and natural organic ligands. *Journal of Hazardous Materials* 2012, 219, 1-12.
- Sipos, P.; Nemeth, T.; Kis, V.; Mohai, I., Sorption of copper, zinc and lead on soil mineral phases. *Chemosphere* 2008, 73, (4), 461-469.
- Smith, E.; Kempson, I.; Juhasz, A.; Weber, J.; Rofe, A.; Gancarz, D.; Naidu, R.; McLaren, R.; Gräe, M., In Vivo-in Vitro and XANES Spectroscopy Assessments of Lead Bioavailability in Contaminated Periurban Soils. *Environmental Science & Technology* 2011, 45, (14), 6145.
- Solt, M.; Deocampo, D.; Norris, M., Spatial Distribution of Lead in Sacramento, California, USA. *International Journal of Environmental Research and Public Health* 2015, 12, (3), 3174-3187.
- Steeffel, C.; Appelo, C.; Arora, B.; Jacques, D.; Kalbacher, T.; Kolditz, O.; Lagneau, V.; Lichtner, P.; Mayer, K.; Meeussen, J.; Molins, S.; Moulton, D.; Shao, H.; Simnek,

- J.; Spycher, N.; Yabusaki, S.; Yeh, G., Reactive transport codes for subsurface environmental simulation. *Computational Geosciences* 2015, 19, (3), 445-478.
- Steffen, W., Welcome to the Anthropocene. *Australasian Science* 2016, 37, (2), 28-29.
- Stewart, L.; Farver, Jr.; Gorsevski, P.; Miner, J., Spatial prediction of blood lead levels in children in Toledo, OH using fuzzy sets and the site-specific IEUBK model. *Applied Geochemistry* 2014, 45, 120-129.
- Strawn, D. G.; Sparks, D. L., Effects of soil organic matter on the kinetics and mechanisms of Pb(II) sorption and desorption in soil. *Soil Science Society of America Journal* 2000, 64, (1), 144-156.
- Su, X.; Zhu, J.; Fu, Q.; Zuo, J.; Liu, Y.; Hu, H., Immobilization of lead in anthropogenic contaminated soils using phosphates with/without oxalic acid. *Journal of Environmental Sciences* 2015, 28, 64-73.
- Tandy, S.; Healey, J. R.; Nason, M. A.; Williamson, J. C.; Jones, D. L., Remediation of metal polluted mine soil with compost: Co- composting versus incorporation. *Environmental Pollution* 2009, 157, (2), 690-697.
- Taylor, M. P.; Camenzuli, D.; Kristensen, L.; Forbes, M.; Zahran, S., Environmental lead exposure risks associated with children's outdoor playgrounds. *Environmental Pollution* 2013, 178, 447-454.
- Tessier, A.; Fortin, D.; Belzile, N.; Devitre, R. R.; Leppard, G. G., Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: Narrowing the gap between field and laboratory measurements. *Geochimica et Cosmochimica Acta* 1996, 60, (3), 387-404.
- Tiberg, C.; Gustafsson, J. P.; Sjostedt, C.; Persson, I., Phosphate effects on copper and lead sorption to ferrihydrite. In *London, United Kingdom: Mineralogical Society: London*, 2012; Vol. 76, p 2456.
- Traina, S.; Laperche, V., Contaminant bioavailability in soils, sediments, and aquatic environments. *Proceedings of the National Academy of Sciences of the United States of America* 1999, 96, (7), 3365-3371.
- Trivedi, P.; Dyer, J.; Sparks, D., Lead sorption onto ferrihydrite. 1. A macroscopic and spectroscopic assessment. *Environmental Science & Technology* 2003, 37, (5), 908-914.
- Uchimiya, M.; Lima, I. M.; Thomas Klasson, K.; Chang, S.; Wartelle, L. H.; Rodgers, J. E., Immobilization of Heavy Metal Ions (Cu II , Cd II , Ni II , and Pb II) by Broiler Litter-Derived Biochars in Water and Soil. *J. Agric. Food Chem.* 2010, 58, (9), 5538-5544.

- USGS, The National Geochemical Survey - database and documentation: U.S. Geological Survey Open-File Report 2004-1001. U.S. Geological Survey: Reston, VA, 2004.
- Vantelon, D.; Lanzirotti, A.; Scheinost, A.; Kretzschmar, R., Spatial Distribution and Speciation of Lead around Corroding Bullets in a Shooting Range Soil Studied by Micro-X-ray Fluorescence and Absorption Spectroscopy. *Environmental Science & Technology* 2005, 39, (13), 4808-4815.
- Vermeer, A. W. P.; Koopal, L. K., Charge Adjustments upon Adsorption of a Weak Polyelectrolyte to a Mineral Oxide: The Hematite-Humic Acid System. *Journal of Colloid And Interface Science* 1999, 212, (1), 176-185.
- Vidal, M.; Santos, M. J.; Abrão, T.; Rodríguez, J.; Rigol, A., Modeling competitive metal sorption in a mineral soil. *Geoderma* 2009, 149, (3), 189-198.
- Von Lindern, I.; Spalinger, S.; Petroysan, V.; Von Braun, M., Assessing remedial effectiveness through the blood lead : soil/ dust lead relationship at the Bunker Hill Superfund Site in the Silver Valley of Idaho. *Science Of the Total Environment* 2003, 303, (1-2), 139-170.
- Walraven, N.; Bakker, M.; van Os, B. J. H.; Klaver, G. T.; Middelburg, J. J.; Davies, G. R., Factors controlling the oral bioaccessibility of anthropogenic Pb in polluted soils. *Science of the Total Environment* 2015, 506-507, 149-163.
- Walraven, N.; Bakker, M.; van Os, B.; Klaver, G.; Middelburg, J.; Davies, G., Pollution and Oral Bioaccessibility of Pb in Soils of Villages and Cities with a Long Habitation History. *International Journal of Environmental Research and Public Health* 2016, 13, (2), 1-23.
- Wang, C.; Lazouskaya, V.; Fuller, M.; Caplan, J.; Schaefer, C.; Jin, Y., Dissolution of Microscale Energetic Residues in Saturated Porous Media: Visualization and Quantification at the Pore-Scale by Spectral Confocal Microscopy. *Environmental Science & Technology* 2011, 45, (19), 8352.
- Weber, J. S.; Goyne, K. W.; Luxton, T. P.; Thompson, A. L., Phosphate Treatment of Lead- Contaminated Soil: Effects on Water Quality, Plant Uptake, and Lead Speciation. *Journal of Environmental Quality* 2015, 44, (4), 1127.
- White, P. D.; Marcus, A. H., The Conceptual Structure of the Integrated Exposure Uptake Biokinetic Model for Lead in Children. *Environmental Health Perspectives* 1998, 106, 1513-1530.
- Wright, S.; Fuller, S.; Jones, S.; McKinney, A.; Rupard, S.; Shaw, S. D. Surficial Geologic Map of the Burlington, Vermont 7.5 Minute Quadrangle; Department of Environmental Conservation: Waterbury, Vermont, 2009.

- Wu, J.; Edwards, R.; He, X. E.; Liu, Z.; Kleinman, M., Spatial analysis of bioavailable soil lead concentrations in Los Angeles, California. *Environmental Research* 2010, 110, (4), 309.
- Wu, J.; Norvell, W. A.; Welch, R. M., Kriging on highly skewed data for DTPA-extractable soil Zn with auxiliary information for pH and organic carbon. *Geoderma* 2006, 134, (1 2), 187.
- Xia, K.; Bleam, W.; Helmke, P. A., Studies of the nature of Cu²⁺ and Pb²⁺ binding sites in soil humic substances using x-ray absorption spectroscopy. *Geochimica et Cosmochimica Acta* 1997, 61, (11), 2211-2221.
- Xie, T.; Reddy, K.; Wang, C.; Yargicoglu, E.; Spokas, K., Characteristics and Applications of Biochar for Environmental Remediation: A Review. *Critical Reviews in Environmental Science and Technology* 2015, 45, (9), 939-939.
- Yesilonis, I. D.; Pouyat, R. V.; Neerchal, N. K., Spatial distribution of metals in soils in Baltimore, Maryland: Role of native parent material, proximity to major roads, housing age and screening guidelines. *Environmental Pollution* 2008, 156, 723-731.
- Yoon, J. K.; Cao, X.; Ma, L. Q., Application Methods Affect Phosphorus-Induced Lead Immobilization from a Contaminated Soil. *Journal of Environmental Quality* 2007, 36, (2), 373-378.
- Young, A., EPA fails to revise key lead-poisoning hazard standards. *USA Today* 2013.
- Zheng, J.; Huynh, T.; Gasparon, M.; Ng, J.; Noller, B., Human health risk assessment of lead from mining activities at semi-arid locations in the context of total lead exposure. *Environmental Science and Pollution Research International* 2013, 20, (12), 8404.
- Zhu, X.; Yang, F.; Wei, C.; Liang, T., Bioaccessibility of heavy metals in soils cannot be predicted by a single model in two adjacent areas. *Environmental Geochemistry and Health* 2016, 38, (1), 233-241.
- Zia, M. H.; Codling, E. E.; Scheckel, K. G.; Chaney, R. L., In vitro and in vivo approaches for the measurement of oral bioavailability of lead (Pb) in contaminated soils: A review. *Environmental Pollution* 2011, 159, (10), 2320.

CHAPTER 6: Supplemental Figures

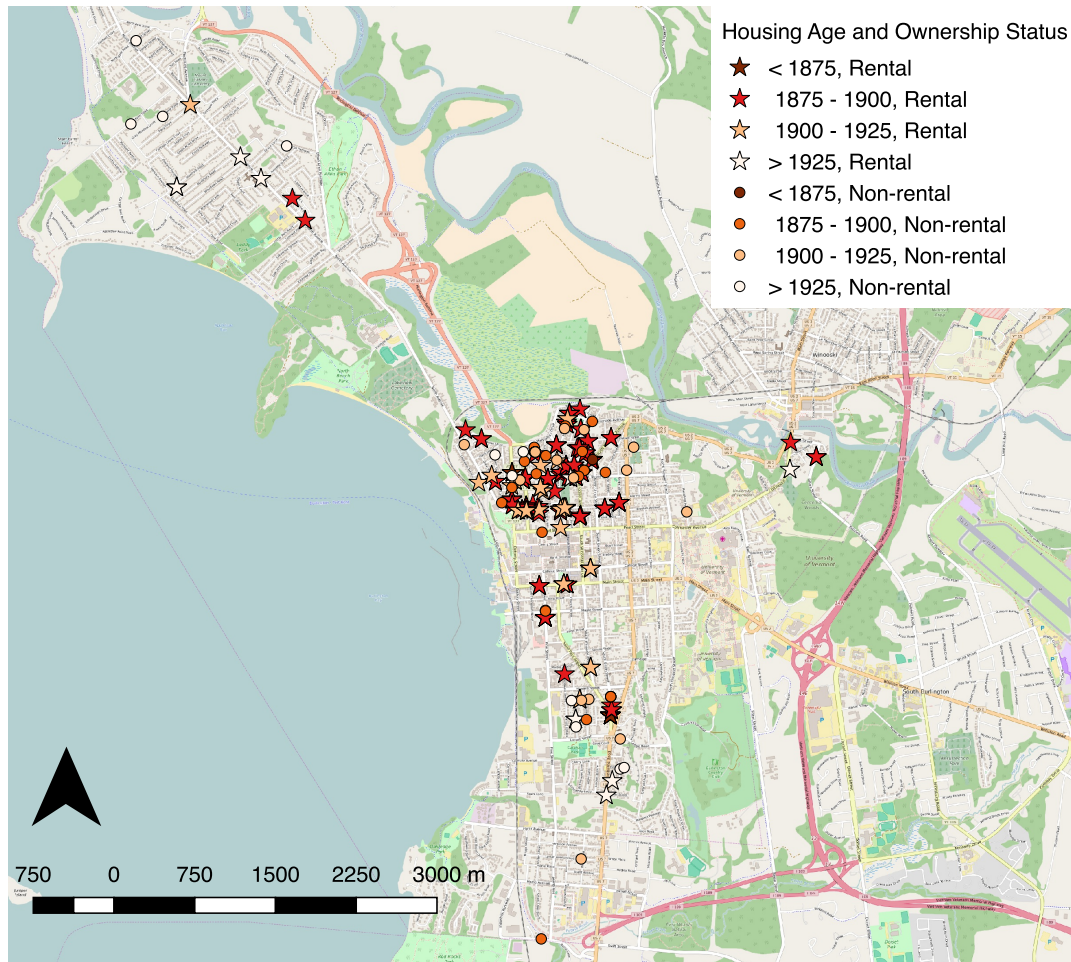


Figure 1. Location of sites remediated by the Burlington Lead Program, symbolized according to age of housing and ownership status. Data obtained from the City of Burlington, visualized using QGIS and OpenStreetMaps.

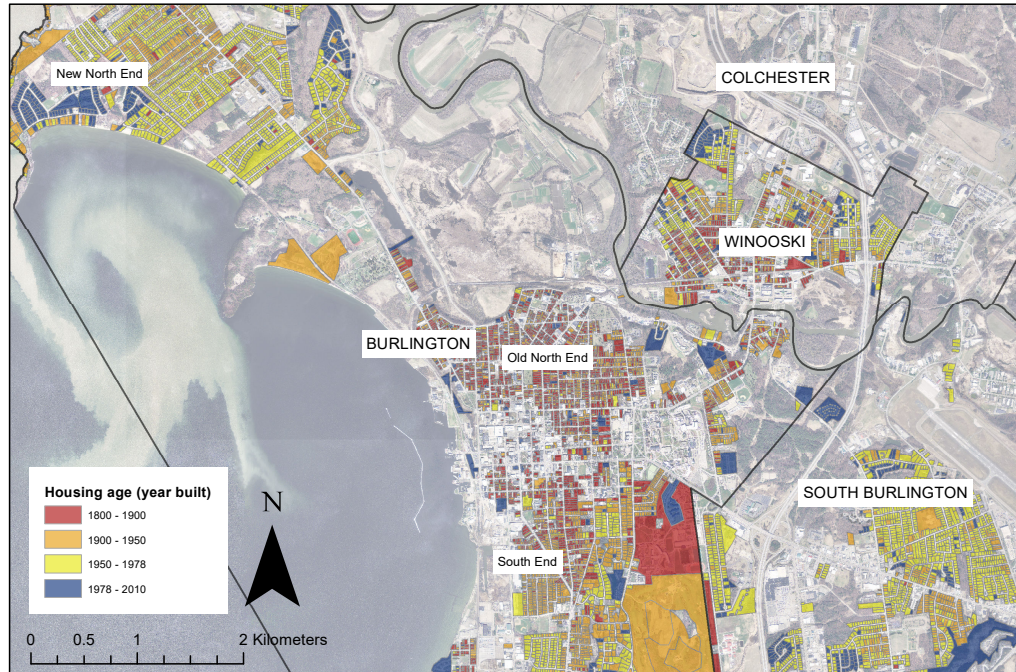


Figure 2. Housing age of residential parcels in Burlington and surrounding areas of Chittenden County.



Figure 3. Site-specific IDW interpolation map showing differences in bioaccessibility at two structures, with measured values given by circles and predicted symbolized with contours.

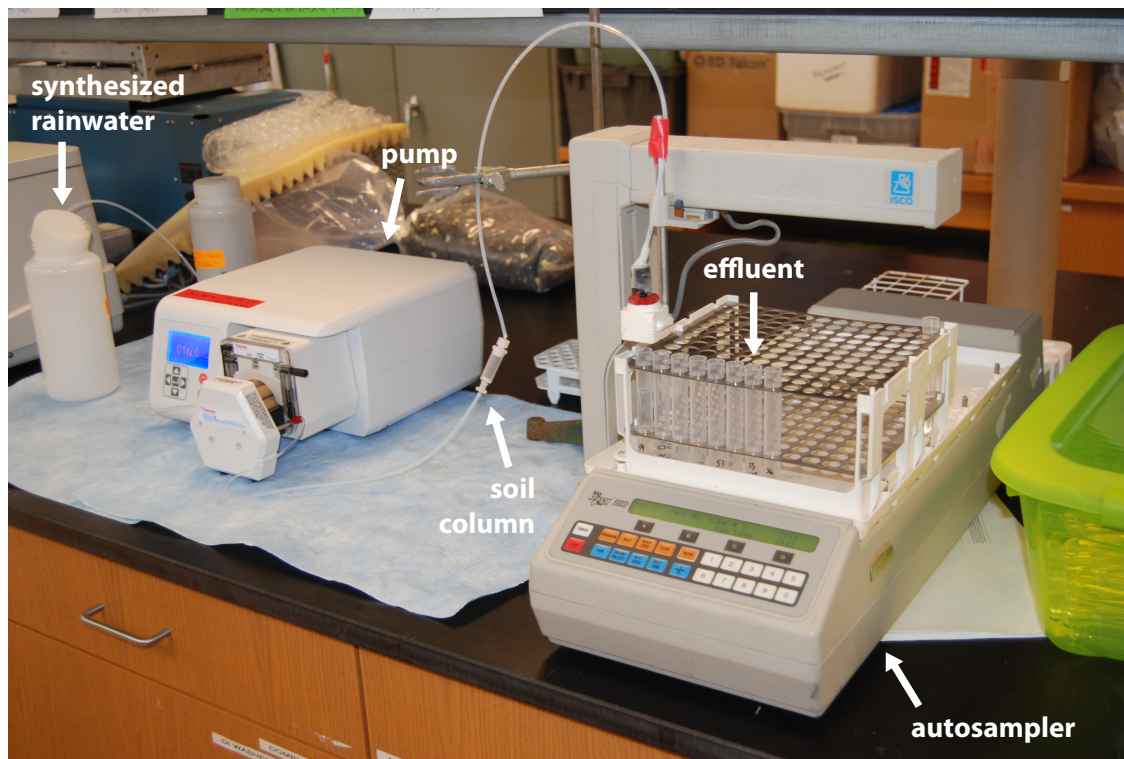


Figure 4. Experimental setup and configuration of flow-through column experiments.

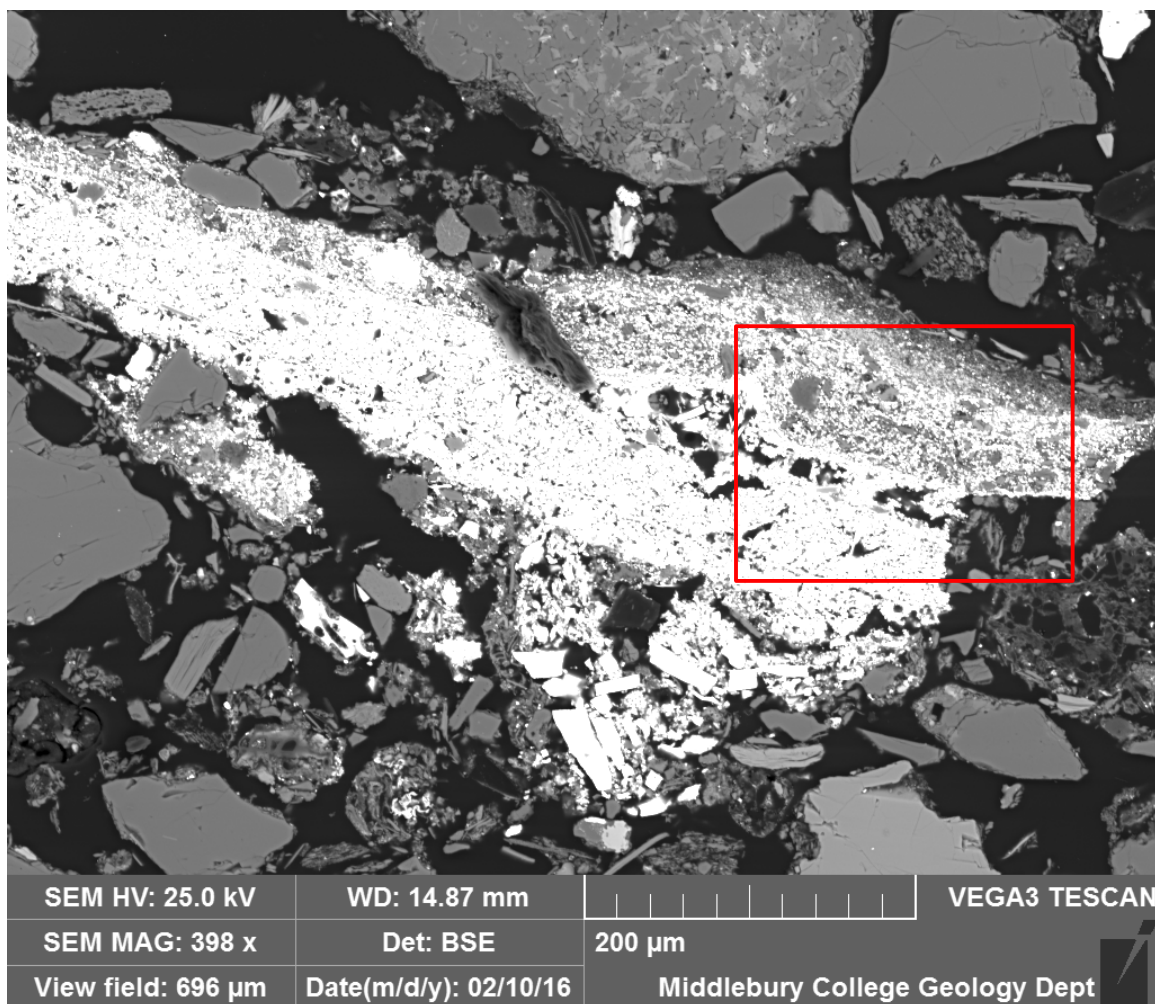


Figure 5. Zoomed-out SEM image encompassing area where SEM-EDS was conducted in Chapter 3, Figure 7, with Figure 7 extent demarcated by red boundary box.

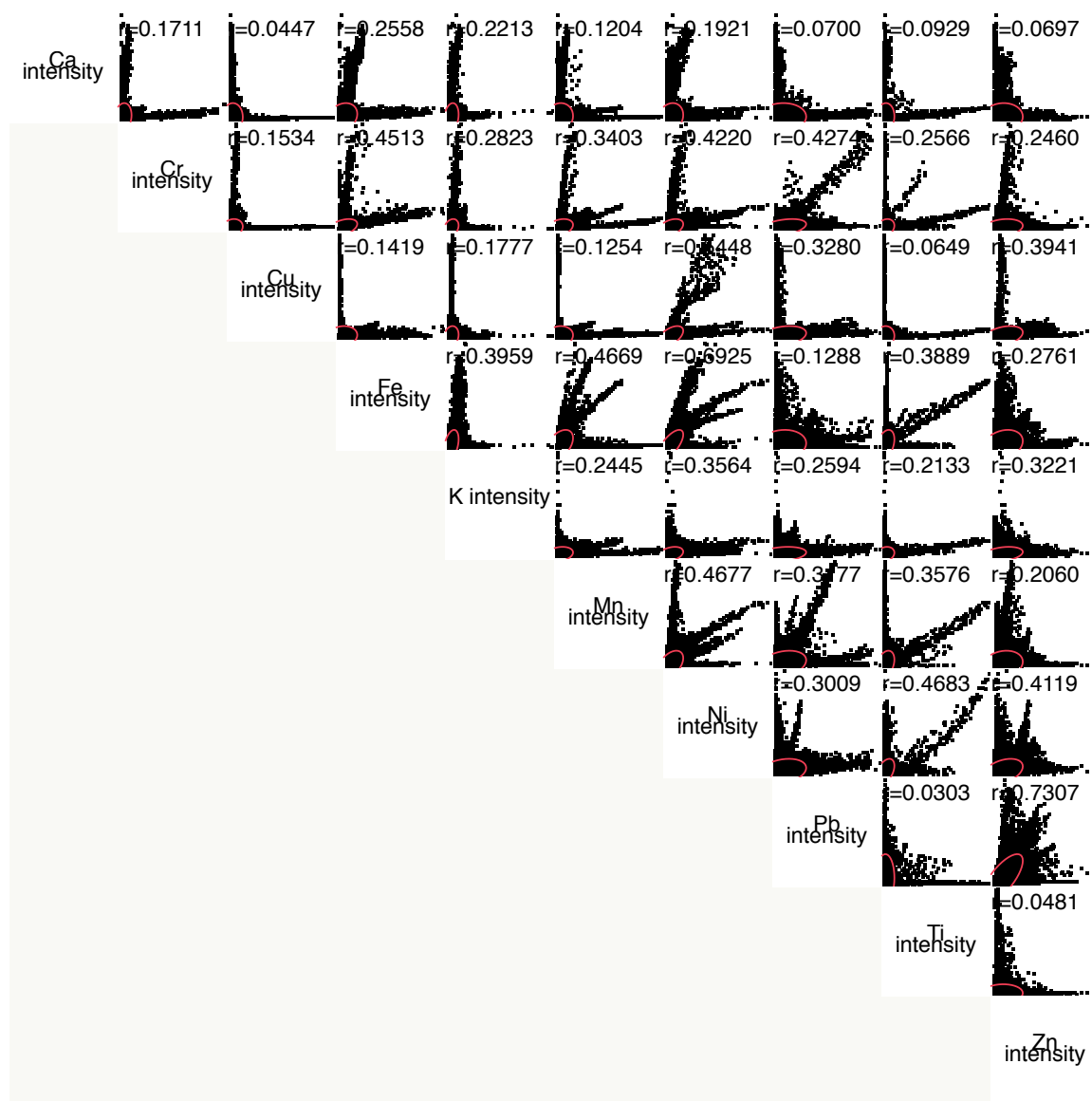
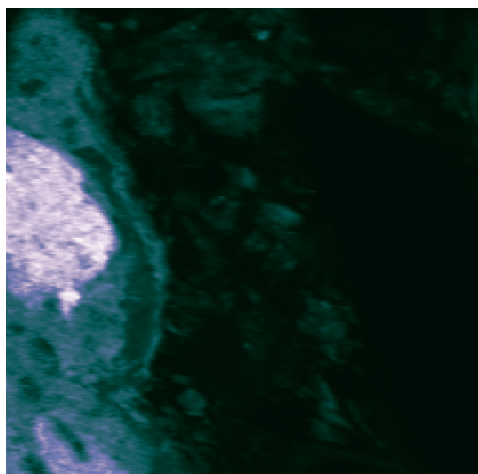
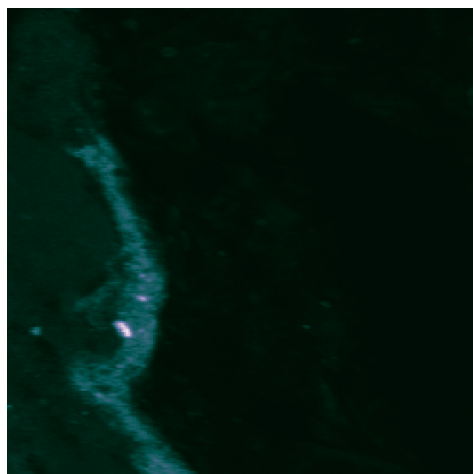


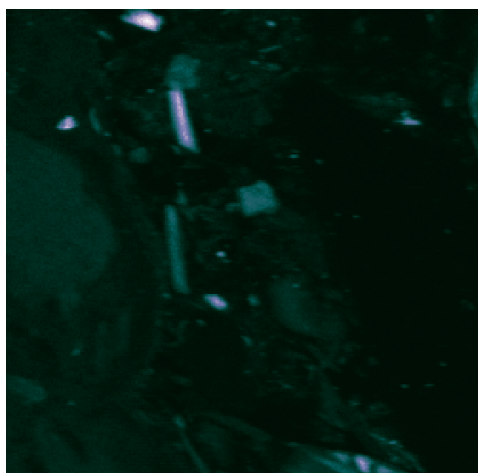
Figure 6. Elemental correlations for μ XRF map 17-01 (unleached soil), with r correlations given in top of each box.



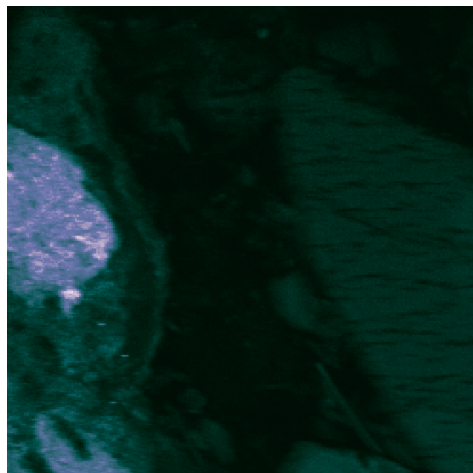
Pb



Zn



Fe



U

Figure 7. Expanded synchrotron-collected μ XRF maps of column leached with PO₄-amended rainwater depicted in Chapter 3, Figure 6, with lighter shades corresponding to fluorescence: Pb, Zn, Fe and U. U is included as it fluoresces in trace quantities within the polygonal mineral (probably a feldspar) on the right side of the map, rendering this mineral visible.